NANOWORLD

An introduction to nanoscience and technology

C N R Rao

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FOREWORD

Nanomaterials have been used by human beings for centuries without knowing the dimensions of the materials they used. The first preparation of nanoparticles in the laboratory was carried out by Michael Faraday as early as 1857. However, it is only in the last ten years or so that the subject of nanoscience and technology has gained importance. This is partly because of the interest in miniaturization of devices. Scientists have also been amazed by the extraordinary properties of materials when they have nanodimensions.

Nanomaterials include nanoparticles, nanowires, nanotubes, nanofilms and so on, of which the carbon nanotubes have become highly popular. In the last three to four years, graphene has made big news in physics, chemistry and materials science. In view of the great current interest and popularity of the subject, we felt that it was important to present the rudiments of nanoscience and technology, understandable by students and beginners, in the form of a small book. I have, therefore, written this little book entitled **Nanoworld** with the hope that it will be used as a popular introduction for young and old alike. This is obviously not a text book. However, the material in this book is sufficient to give an idea of the nature of nanoscience and technology and all its facets, including preparation, properties, phenomena and applications. I do hope that the book will be found useful by students, teachers and others who are desirous of learning something of this exciting subject of great current interest.

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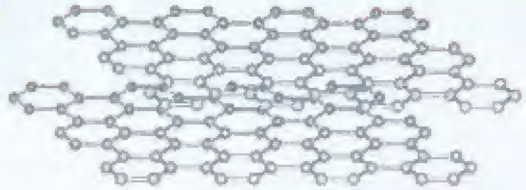


NANOWORLD

An introduction to nanoscience and technology

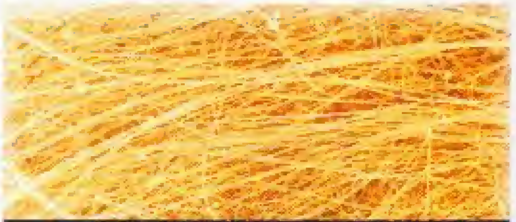
Objectives

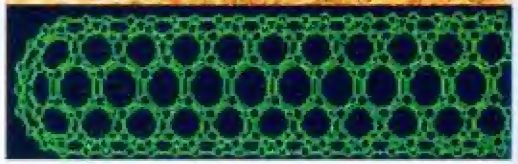
This book is meant for students, teachers and all those who desire an introduction to nanoscience and technology. We shall, therefore briefly present some basic aspects of nanoscience and technology.

- We shall first introduce various types of nanomaterials with examples and describe some of their properties.
- We shall then describe a few simple experiments for making and characterizing nanomaterials.
- We shall end by describing applications in various areas including electronics, biology and medicine.

1. Introduction

Nano is the flavour of the day. The nanoworld deals with tiny objects which are nanometric in size at least in one dimension. The science of nanomaterials deals with their generation and properties and the phenomena exhibited by them because of their small size. Nano-objects can be spherical, wiry, tubular or sheet like.





Carbon nanotubes, for example, are tubular materials. Although nanoscience and technology are topics of recent origin, nanomaterials themselves have been known for a long time. The term nanotechnology is commonly used now-a-days by people and the press. The subject of nanoscience and technology has gained great importance because of the potential applications in various areas such as chemical and textile industries, materials industry, medical diagnostics, drug and gene delivery and electronics.

2. History of Nanomaterials

The history of nanomaterials can be traced back to the Roman period. Even at that time, colloidal metals were used to dye

fabrics, color glass and to treat arthritis. The popular dye, The Purple of Cassius, formed on reacting stannic acid with chloroauric acid is actually made up of tin oxide and gold nanoparticles. Romans were adept at impregnating glass with metal particles to achieve dramatic effects. The Lycurgus cup is an outstanding example of this. It appears red in transmitted light, and green in reflected light. Maya blue used by the Mayas consists of indigo, silica and metal and oxide nanocrystals. Clearly, the ability to synthesize nanocrystals preceded the understanding of the nanoscale phenomena.

The Lycurgus Cup

This beautiful cup is perhaps the only surviving and undamaged example of a very special type of glass, dichroic glass. The special character of this glass is that it changes colour when the cup is held up to light. The cup

is opaque green but when light is shone through it, it turns to a glowing translucent red cup as if by magic. These unique optical properties are due to the small amounts of colloidal gold and silver present in the cup.

The cup is an example of 'cage-cup' method of glass making. First, a thick glass blank was made by blowing or casting to make the cup. The thick glass blank cup was ground carefully until only the desired figures remained in high relief. In the Lycurgus Cup, some parts of the beautiful figures are almost standing free from the surface of the cup and are held in position and connected to the cup's surface only by bridges. An episode from the myth of Lycurgus, a king of the Thracians (around 800 BC) is the theme of the scene on the cup. Ill-tempered Lycurgus attacked Dionysos and his companion Ambrosia. Ambrosia appealed to Mother Earth for help. Mother Earth turned Ambrosia into a vine. Thus transformed, Ambrosia held Lycurgus captive by coiling herself around the cruel king.

The cup depicts Lycurgus trapped by the branches of the vine and tormented by Dionysos for his cruelty. Many suggest that the theme of the myth of the triumph of Dionysos over Lycurgus probably refers to the victory of Constantine over emperor Licinius in 324 AD.

Michael Faraday and "divided metals"

In 1612, Antonio Neri, a priest and a glass maker of Florence in Italy, published a treatise titled "L'Arte Veraria" in which he described the synthesis of colloidal gold. John Kunckel of Germany translated this treatise into German in 1689.

It was in 1857 that Michael Faraday carried out path breaking work on what he called "divided metals". Faraday identified the essential nature of colloidal (nanoscale) metal particles.

Michael Faraday

He stated "gold is reduced in exceedingly fine particles which becoming diffused, produce a beautiful fluid...... the various preparations of gold whether ruby, green, violet or blue ....consist of that substance in a metallic divided state".

Michael Faraday's colloids

The gold particles prepared by Faraday are still preserved in the Royal Institution in London.

The story of the Damascus sword

The story of the Damascus sword is truly remarkable. Damascus swords were first made in the eighth century.

They were famous for their strength and sharpness. It is said that the blade of Damascus sword could cut a piece of silk as it fell to the ground and at the same time retain their sharpness even after cutting through stone or metal or other swords.

What gave the sword its uniqueness? The technique for making the sword was lost for centuries and the secret of the sword remained unknown until recently.

Dagger made from wootz steel

Peter Paufler at the Technical University in Dresden, Germany and his colleagues used an electron microscope and studied samples from the blade of the Damascus sword made in the 17th century. They found tiny nanowires and nanotubes in the sample.

Complex surface patterns in a Damascus sword

According to the paper published by them in Nature, further studies revealed the first ever carbon nanotubes present in steel. Medieval sword-smiths of the region were unknowingly using nanotechnology to give strength and flexibility to the sword.

The swords were forged from Wootz steel first made in India as early as 300 BC. Peter Paufler and his colleagues discovered that Wootz has a microstructure of nanometric-sized tubes just like nanotubes. They think that Wootz steel from India contained transition-metal impurities. They believe that at high temperatures, these impurities could have catalysed the growth of nanotubes from carbon provided by their burning wood.

3. How is the nanoworld different from the world around us?

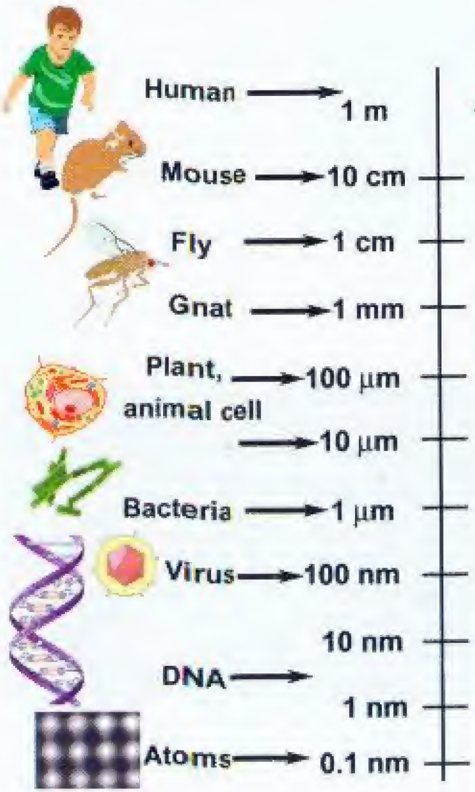
In the nanoworld, we cannot see objects with our naked eyes, we cannot touch or manipulate them by our hands or by any of the tools that we generally use. The objects that we deal with in the nanoworld are very tiny and are close to the size of atoms and molecules. The effects of gravity and inertia are less dominating in the nanoworld, but surface tension and other molecular forces do play a role.

Nanoworld is also different from the world of space and galaxies where we probe vast celestial objects with enormous

size and mass. We use sophisticated telescopes to look at them.
Nanoworld is just the opposite. Here, we use various types of microscopes.

What is "nano" ?

Nano in Greek means "dwarf", but nano is infinitely smaller than a dwarf. It is one billionth of a meter or 10^{-9}m.



Nanometer is the scale used to measure objects in the nanoworld.

Let us work out a table.

1 cm = 10^{-2}m.

1 mm = 10^{-3}m.

1 micrometer = 10^{-6}m.

1 nanometer = 10^{-9}m.

Macroscale is more than 100 nm. Mesoscale is between 10 and 100 nm.

Remember that distances between atoms in molecules are measured in Angstroms (Å). 1 Angstrom (Å) = 0.1 nm.

Let us compare nano objects with familiar objects

Comparing an object with a diameter of a nanometer to that of a meter is like comparing the size of a small marble to the size of the earth!! Some have jocularly suggested that a nanometer is the length a man's beard grows in the time he takes to raise the razor to his face.

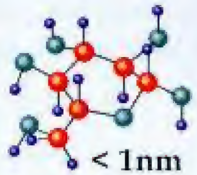
A few more familiar examples may convince you of the difficulty in imagining the size of nano-objects. A single strand of human hair is around 20,000 nanometers in diameter.

The population of India is one billion or 100 crores. Each Indian - you or me - is nano in comparison with the total population of India.

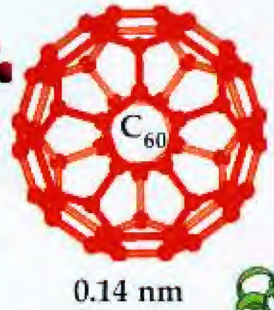
Now, let us look at the size of a nanometer from the opposite angle. If one lines up 10 hydrogen atoms

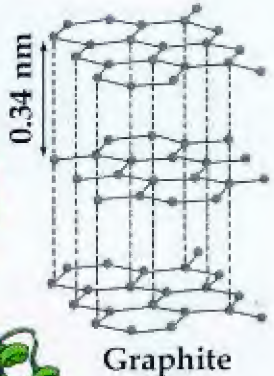
next to each other, the resulting length would be roughly 1 nanometer.

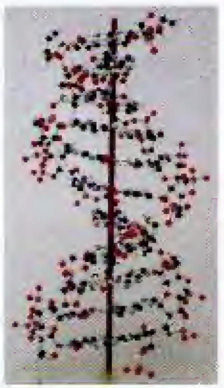
The diameter of a hydrogen atom is ~0.1 nm. The bond distance between carbon atoms in diamond is 0.154 nm or 1.54Å. The bond distance between carbon atoms in C_{60} is 0.14 nm or 1.4Å. The bond distance between carbon atoms in graphite is 0.14 nm or 1.4Å.



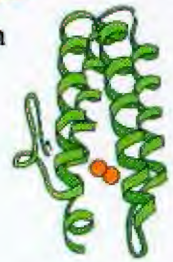
Glucose is below 1nm.







The width of a DNA molecule is ~2.5 nm.



The diameter of a protein or virus is around 10 nm or less.

It should now be abundantly clear that we are dealing with extremely minute sizes when we enter the nanoworld.

4.0 Beginning of nanoscience

"There's plenty of room at the bottom" (Feynman)

The beginning of nanoscience is traced to a lecture Richard P Feynman, the famous physicist, gave in 1959 at the annual meeting of the American Physical Society held at The California Institute Of Technology, U.S.A. In his introduction to the topic of his lecture, he said "I would like to describe a field in which little has been done but in which an enormous amount can be done in principle. This field .... will not tell us much of fundamental physics but.... it might tell us much of great interest about the strange phenomena that occur in complex situations. What I want to talk about is the problem of manipulating and controlling things on a small scale. It is a staggeringly small world that is below. In the year 2000, when they look back, they will wonder why it was not until the year 1960 that anybody began to move in this direction".

Richard Feynman (1918 - 1988)

Feynman was one of the most publicly well known physicists even during his lifetime as much for his outstanding contributions to physics as for his brilliant teaching, his lectures, sense of humor and his multi-faceted talents. He is famous for his work in the theory of quantum electrodynamics, Particle physics and the physics of superfluidity of supercooled liquid helium. He shared the Nobel Prize for Physics in 1965 with

Schwinger and Tomonaga for quantum electrodynamics. He is also well known for "Feynman diagrams", pictorial representations of mathematical expressions that govern the behaviour of subatomic particles. He participated in the Manhattan Project, was a member of the group that investigated the disaster of Space Shuttle Challenger. In addition to his outstanding work in theoretical physics, he pioneered the work in quantum computing. He was involved in developing a new method of using a number of computers to solve complex problems (parallel computing).

Feynman was famous as a teacher. He strongly believed that if a topic could not be explained satisfactorily in a freshman lecture, then it was not understood fully by the lecturer. Feynman was specially proud of the Oersted Medal for teaching that he received.

He was a free spirit. Among his multiple talents was lock picking! His was a multi-faceted personality - he was an amateur painter, drum player and was keenly interested in biology, art and Maya hieroglyphics.

Feynman was known for his sense of humor which he inherited from his mother. He was also a great prankster. His biographer called him "All genius, all buffoon".

"Why cannot we write the 24 volumes of Encyclopaedia Brittanica on the head of a pin?"

During the course of his lecture, Feynman posed this question and proceeded to outline a perfect blueprint for how to proceed in this new field. He anticipated the following problems and suggested the possible solutions:

Problem 1: How to put 24 volumes of the encyclopaedia on a pin head?

Solution: Reduce the size or demagnify.

Problem 2: How to write small?

Solution: Write in raised letters of metal and prepare a silica template using light.

Problem 3: How to read the writing invisible to the naked eye?

Solution: Build powerful microscopes.

Problem 4: How to have identical copies?

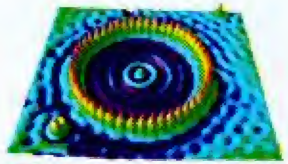
Solution: Use the silica template to make any number of identical copies.

Feynman's predictions

Feynman predicted that it would be possible to put all the printed books in the world on a single library card in ten years from then. This has almost become a reality with the million books project!

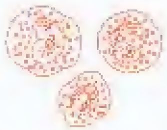
Feynman covered various aspects of nanoscience and technology in his lecture:

- the need for electron microscopes,
- miniaturising the computer,
- using evaporation as a means of miniaturising,
- developing miniature tools to manipulate nano-objects at the atomic level (a master-slave system).



STM image of a quantum corral (courtesy: IBM Research division)

Is nanoscience and technology an attempt to mimic Nature?



Nature offers many successful examples of nano-objects at work. If we have to build machines with components on a cellular scale, we need to develop new materials and new technologies. The invention of the integrated circuit in 1958, advances in micro-electronics, use of photolithography, and invention of sophisticated microscopes have resulted in the miniaturisation of the computer chips. The size of the computer chip decreased from 10,000 nm in 1971 to 65 nm in 2003.

Cells are the perfect examples of busy multi-tasking nanosystems. They are very tiny - just a few nanometers in size. Information is stored in them. They are capable of replicating themselves, move around and also manufacture various substances needed by the organism.

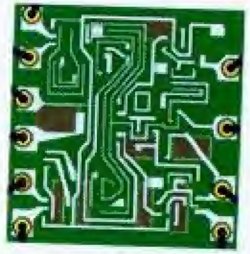
Cells provide the blueprint for developing nanosystems that can do all the tasks at the atomic level that cells perform in a biological system.

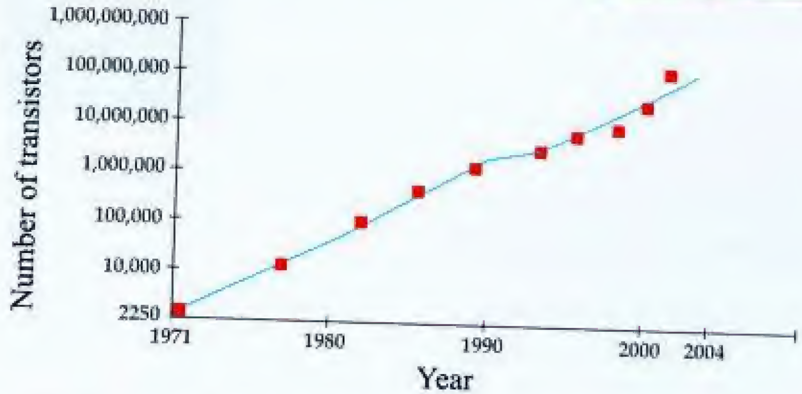
5.0 Moore's Law

Gordon Moore, one of the founders of Intel, made the observation in 1965 that the number of transistors per circuit would double every year, through the decade following that

year. Later he changed this to 24 months. There were only 30 transistors on an integrated circuit at that time.

Carver Mead, a colleague of Moore, called this prediction **"Moore's Law"**.

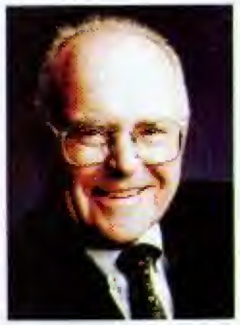




We must remember that Moore's Law is neither a scientific law nor a law of Nature. It is only a prophetic statement! Moore himself had this to say about the law: **"Moore's Law has been the name given to everything that changes exponentially"**.

This exponential change is one of the reasons why nanoscience has become important and relevant today. Nanoscience and technology are today at the same stage as Information Technology was in the 1960s and Biotechnology was in the 1980s. It is predicted that in the years to come, this subject will witness the same type of exponential growth as the other two witnessed earlier.

Gordon Moore (1929 -



Moore co-founded Intel company to manufacture specialised computer memory products in 1968. He was the Executive Vice President till 1975. He was the President and Chief Executive Officer of Intel Corporation from 1979 to 1997.

Moore was mainly responsible for the company to become the unquestioned leader in the semiconductor industry and the largest manufacturer of computer chips in the world. Intel also produced the first microprocessor.

Moore published in 1965 in the Electronics Magazine a paper under the title "Cramming more components onto integrated circuits" where he states "The complexity for minimum component costs has increased at a rate of roughly a factor of two per year ... Certainly over the short term this rate can be expected to continue, if not to increase. Over the longer term, the rate of increase is a bit more uncertain, although there is no reason to believe it will not remain nearly constant for at least 10 years. That means by 1975, the number of components per integrated circuit for minimum cost will be 65,000. I believe that such a large circuit can be built on a single wafer".

Every aspect of digital electronics including the processing speed, memory capacity, resolution of digital cameras and the liquid crystal display screens are all showing the exponential growth predicted by Moore's observation. The phenomenal increase in the number of transistors that can be placed on the integrated circuit is playing a central role in every facet of

modern life. We can safely say that Moore's Law is the driving force behind the growth in the entire Information Technology industry and beyond. Indeed, Moore's Law is not merely an observation or prediction; it also gave a blueprint for the development of the semiconductor industry.

Miniaturization of microprocessors

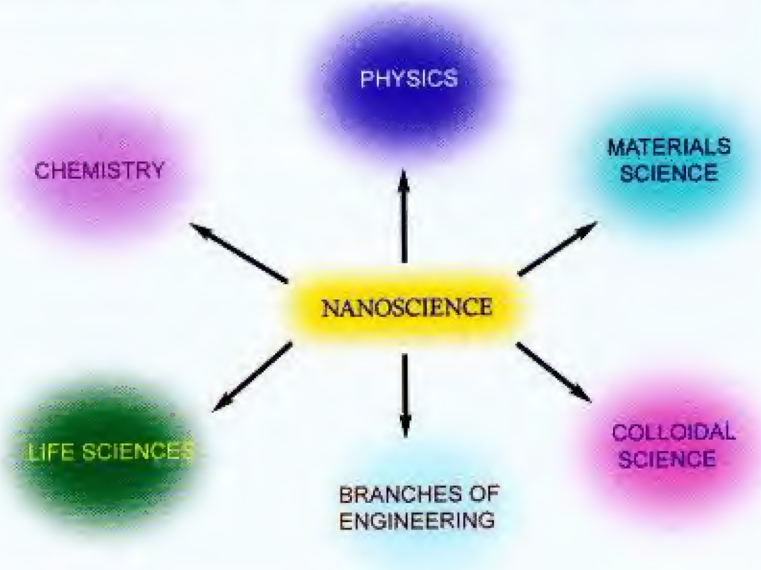
On 12.11.2007, Reuters reported that Intel Corp, the world's biggest microchip maker, announced fast new processors made with techniques that can etch circuitry nearly 200 times smaller than a red blood cell! **The new process used to make the chips is called "the 45 nanometer process"**. The General manager of Intel's enterprise group said "Across all segments we're increasing performance and increasing energy efficiency". Though there is not much fundamental change in the design, they represent an important step in continuing the industry's record of making processors that get smaller and faster every two years or so.

These chips are another example of Intel's successful strategy of shrinking an existing chip design to a smaller size, then next year following it up with an all-new blueprint, known as a **microarchitecture**.

This miniaturization of the chips has also made the microprocessors powered by them much faster. Using 'the 45 nanometer shift' is also important to Intel because it means the company can make more chips from a single platter of silicon.

Nanoscience: The multidisciplinary science

Nanoscience is at the cutting edge of science. It is highly multidisciplinary. It draws from such diverse fields as



6.0 Nanomaterials

Top-down or bottom-up?

Research in nanoscience and applications in nanotechnology use two different approaches - **"bottom-up" and "top-down"**. In the **"bottom-up" approach**, nanomaterials are made from atoms or molecules (small to the big). This approach also uses the principle of molecular recognition and self assembly.

In the **"top-down" approach**, nano-objects are made from larger objects (big to the small).

A bulk material, in this method, is broken up into small particles using grinders, lasers etc.

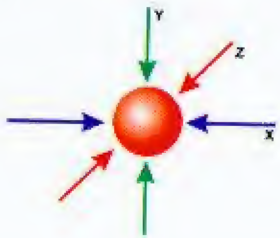
Examples of the bottom-up approach

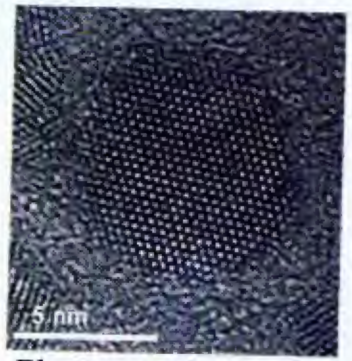
In this approach, larger structures are built atom by atom or molecule by molecule. This approach is involved in forming well-defined structures of DNA.

Using principles of supramolecular chemistry and molecular recognition, molecules can be made to arrange themselves automatically into useful shapes and structures. Similarly, atoms can assemble to form clusters and then nanoparticles.

Different types of nanomaterials

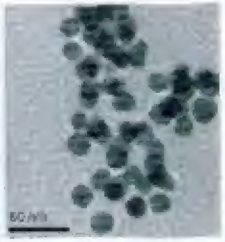
Nanomaterials are of various types. **We have nanoparticles or nanocrystals. Small nanoparticles are often called quantum dots.** These are materials which possess nano-dimensions in all the three directions.

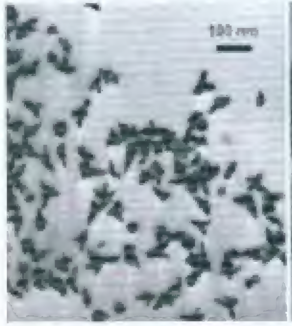


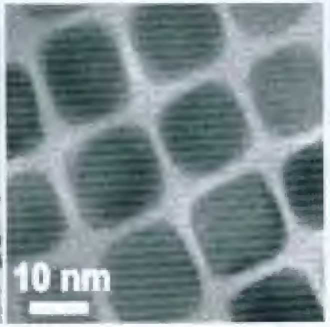


Electron microscope image of a CdSe nanocrystal showing atoms packed closely.

Many of them are spherical and the diameter of these particles will be in the **1-50 nm** range.

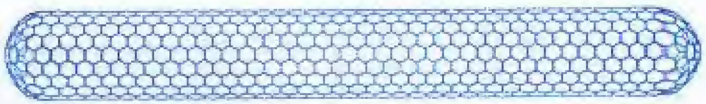






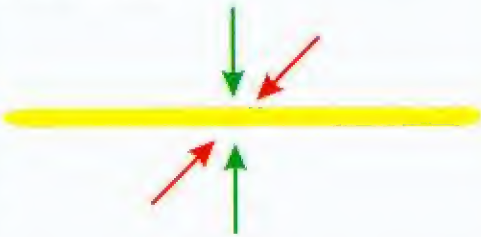
Nanoparticles or nanocrystals of a variety of materials such as metals, metal oxides, semiconducting and magnetic materials have been prepared. They can have different shapes (triangles, squares as shown in the images above).

One-dimensional materials

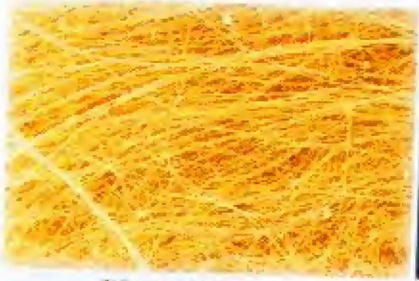


Carbon nanotube

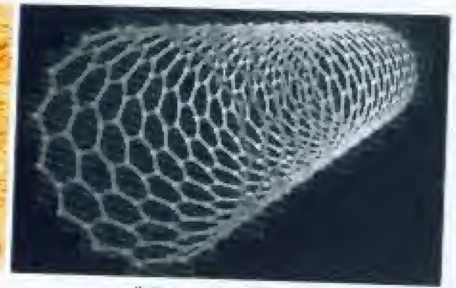
These materials are long (several microns in length) but with diameters of only a few nanometers. Nanowires and nanotubes belong to this category.



Nanowires and nanotubes of metals, oxides and other materials have been made.



Nanowires



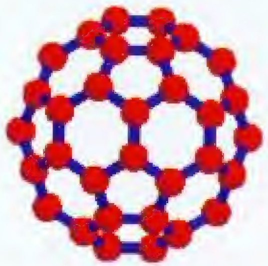
Nanotube

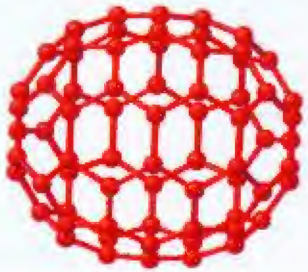
Carbon Nanotubes

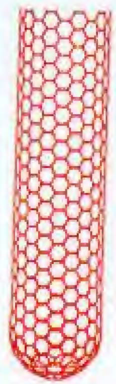
Nature turns carbon into diamonds and graphite, and man turns carbon into nanotubes. Did you know that chimney soot contains carbon nanotubes?

Carbon nanotubes are stronger than steel wires, can conduct thousand times more electricity and can bear weight million times more than their own weight. They conduct heat efficiently.

Carbon nanotubes belong to the fullerene family. Carbon nanotubes can be considered to be extended fullerenes. (Look at the closed end of the nanotube).



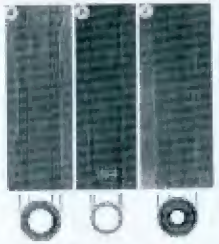




Fullerenes or buckyballs are spherical. Carbon nanotubes are cylindrical.

Carbon nanotubes were first made in the laboratory by **Endo of Japan in 1976**, but **Sumio Iijima** of Japan is credited with the first proper description. Iijima's paper in 1991 generated tremendous interest in carbon nanostructures and opened up a new field of research. He joined NEC of Japan in 1987 where he discovered the carbon nanotubes through electron microscopic images.

In carbon nanotubes, the central tubule generally has a diameter of 1 to 10 nm. Nanotubes of inorganic materials such as metals, oxides and sulfides can also be made in the laboratory.

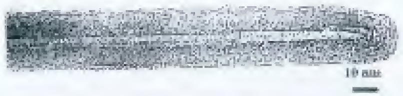


Types of carbon nanotubes

Carbon nanotubes can be **single-walled nanotubes or multi-walled.**

Single-walled nanotubes

Single-walled nanotube



Multi-walled nanotubes

Single-walled carbon nanotubes generally have a diameter of 1-10 nm but the length can be hundreds of nanometers.

Multi-walled carbon nanotubes have layers of graphite surrounding a central tubule of 1-10 nanometer diameter.

Note that single-walled carbon nanotubes have only the tubule (of 1-10 nm diameter) and no graphite layers around it.

Y-junction nanotube

Single-walled carbon nanotubes

These nanotubes are formed by the rolling of a one atom thick sheet of graphite (graphene) into a seamless cylinder with a diameter of ~1 nm. The length to- diameter ratio or aspect ratio of a single walled carbon nanotube is usually more than 10,000.

Depending on the way the sheets get rolled, one obtains nanotubes of different chirality and properties. Also, depending on the way the sheet is rolled, nanotubes can be metallic or semiconducting.

Multi-walled carbon nanotubes

Multi-walled carbon nanotubes consist of multiple layers of graphite where one graphite layer is rolled in on another layer in the shape of a tube. The structures of multi-walled carbon nanotubes can be described using two familiar models - the Russian doll model and the parchment model.

In the Russian doll model, sheets of graphite are arranged one inside another in concentric cylinders of increasing

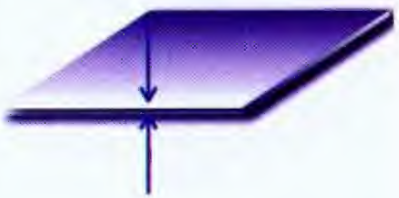
diameters. In the parchment model, a single sheet of graphite is rolled around itself just like a newspaper or parchment is rolled.

Two-dimensional nanomaterials

In addition to nanocrystals, nanowires and nanotubes, we have another class of nanomaterials that are two-dimensional. Nanofilms, nanosheets or nanowalls belong to this category.

Nanowalls

Above, we see a nanofilm consisting of nanoparticles formed at the interface between water and an organic liquid.



The area of nanofilms can be large (several micron^2), but their thickness is very small (only a few nanometers).

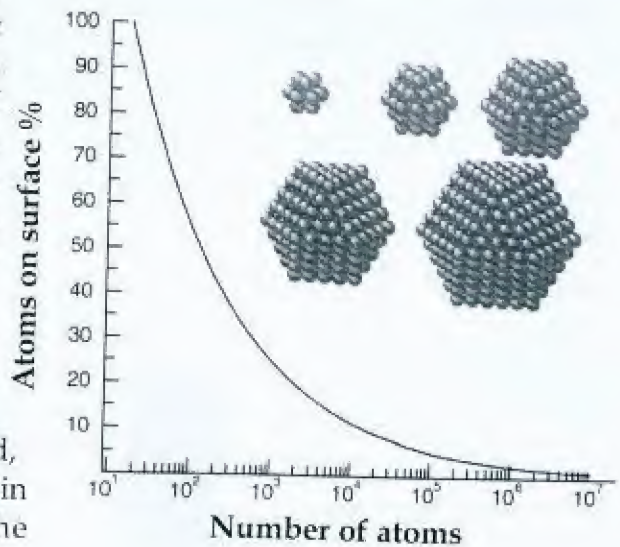
You know that graphite consists of layers of six membered carbon rings. Suppose you lift off just one layer from graphite, you get a graphene sheet. It will be a very thin sheet with a thickness of a few Angstroms.

7.0 Properties of nanomaterials

"Atoms on a small scale behave like *nothing* on a large scale.. ... So, as we go down and fiddle around with atoms down there, we are working with different laws...."

Richard Feynman.

What are the main properties of nanomaterials?



The main feature is that size determines the properties of nanomaterials. When we are dealing with objects in the real world, properties do not change much with size. In the nanoworld, however, change in size affects the

properties enormously. If you go on reducing the size of a material to that of a very, very small particle, say, 1 nm, then all the atoms constituting the particle will be on the surface.

As you increase the size from 1 nm to 2 nm or 5 nm, the number of atoms on the surface will decrease.

Different types of nanomaterials and their sizes

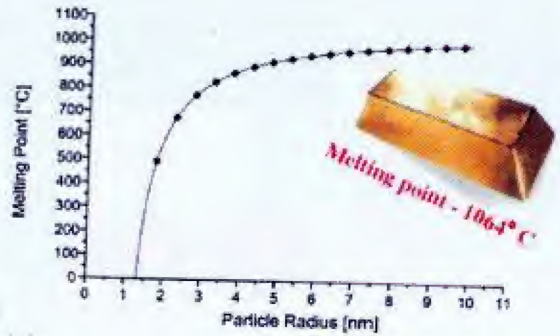
Type of nanomaterial	Material	Diameter /thickness
Nanocrystals	Metals, Inorganic materials such as oxides, nitrides, sulfides etc.	1-50 nm
Nanofilms		1-10 nm
Nanowires	Metals, oxides, nitrides, sulfides.	1-100 nm
Nanotubes	Carbon, metals, inorganic materials.	1-100 nm
Nanoporous solids	Phosphates, zeolites	0.5 - 10 (pore size)
Surfaces	Various materials	1-1000 nm

If you take a material like iron or any material which is magnetic and go on decreasing the size of the particles, the properties

will change. They lose their magnetism when the size is very small.

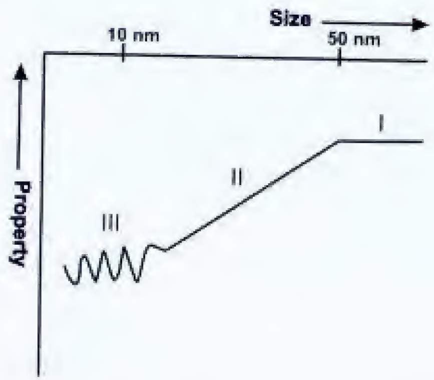
Gold shines as a metal. However, when we make very tiny particles of gold of 1 nm diameter, they are no longer metallic. They do not shine like bulk gold. Bulk gold is not chemically reactive. That is why we make jewellery of gold. Small particles of gold, however, are chemically reactive.

The melting point of a solid changes when we make tiny particles of the material. For example, small particles of gold melt at a much lower temperature than a big piece of gold.



Size of particles and quantum effects

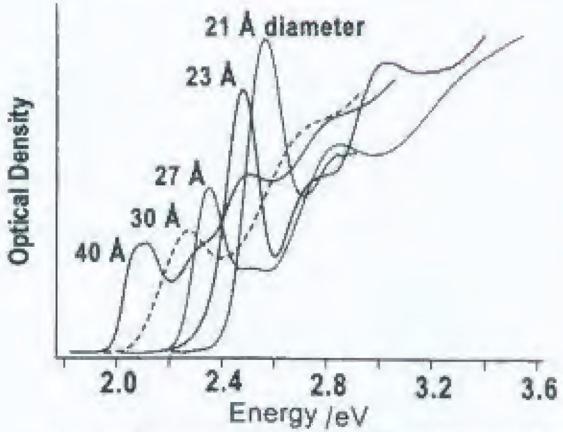
When particles are of a reasonable size, say 50 nm and above, (region I in the figure), their properties will be similar to those of the bulk. When they are a little smaller, say 10- 50 nm, their properties may vary linearly



with size (region II in the figure). However, when the size becomes very small, we get some unusual, new properties (region III in the figure). Here we see quantum effects. In this region, electrons confined in a small volume or a box exhibit energies which depend on the length of the box.

Size-dependent properties of cadmium selenide

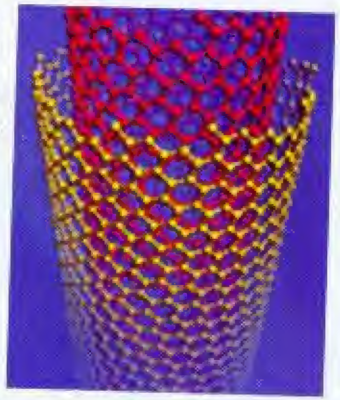
Let us take a material like cadmium selenide. It is a semiconductor. If you shine some light on it, it gives out light of different colours. Let us see this picture showing blue, green, yellow and red coloured lights emitted by CdSe particles.



Emission spectra of CdSe nanocrystals

The red light comes from particles of around 5 nm in diameter and the green light emitting particles would be around 3 nm in diameter.

Carbon nanotubes and graphene



Carbon nanotubes are some of the strongest materials. It is jokingly said that if you want to reach heaven by a lift, you must use carbon nanotubes as ropes to pull the lift!

Depending on the structure, nanotubes behave like a metal or like a semiconductor. This depends on the way the graphene sheet rolls to form the nanotube. Properties of nanotubes depend on the diameter.

Graphene, the two dimensional nanocarbon, is found to have extraordinary properties. Electrons in graphene move differently from other solids and show unusual effects. Graphene has been used to make sensors, electrochemical devices and transistors. In the last 3-4 years, graphene has become a hot topic of research.

8.0 Seeing nano-objects

It was mentioned earlier that objects of nanometric size cannot be seen by naked eyes. Neither can we see them by ordinary microscopes. The need for special microscopes to see nano-objects resulted in a number of special microscopes in recent years.

Transmission Electron Microscope (TEM), **Scanning Electron Microscope** (SEM), **Scanning Tunnelling Microscope** (STM)

and **Atomic Force Microscope** (AFM) are all essential for the study of nanomaterials.

Microscopes that made the difference

Transmission Electron Microscope and Scanning Electron Microscope have been in existence for a few decades. **TEM** is like photography but done in vacuum with an electron beam of wavelength smaller than the size of an atom (~0.1 Å).

In SEM, a pointed electron beam traces the surface collecting the backscattered electrons from each point. Being gentle with the surface in contrast to TEM, SEM can be carried out under near ambient conditions, with moderate electron energies (few keV). In TEM, the electron beam pierces through the thin slice of matter before capturing the image. These two techniques are complementary in style and operation.

With a good Scanning Electron Microscope, we can generally see objects of the size of 50 nm. With a good Transmission Electron Microscope, we can see objects of 2 or 3 Angstroms. Remember, 1 Angstrom is 0.1 nanometer.

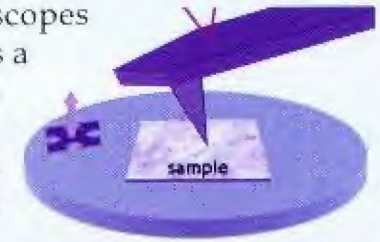
Scanning Tunnelling Microscope (STM) and Atomic Force Microscope (AFM)

STM and AFM can be used to see very small objects (from a fraction of a nanometer to tens of nanometers) and study some of their properties. But for the technological advancement in piezo-drivers, nanometer scale motion would not have been possible.

Gerd Binnig

Heinrich Rohrer

Scanning Tunnelling Microscope (STM) and Atomic Force Microscope (AFM), are the result of the innovative work of Gerd Binnig and Heinrich Rohrer in the 1980s. Gerd Binnig and Heinrich Rohrer, inventors of STM and AFM received the Nobel Prize in 1986. Both the microscopes use a sharp tip as a probe to trace fine topological contours of the surface of an object. They are, therefore, called scanning probe microscopes.



Binnig joined the IBM research laboratory at Zurich, Switzerland in 1978. He worked with Rohrer and developed the design for Scanning Tunnelling Microscope. In 1994 Professor Gerd Binnig founded Definiens which provides analysis and interpretation of images on every scale - from images of microscopic cell structures to satellite images. Use of Definiens' technology helps to maximize the value of the images and thereby arrive at better decisions. Definiens now focusses on applications for Life Sciences and Earth Sciences. Definiens' technology is used to accelerate research in drug discovery and diagnostics processes. This technology is also used to classify and analyse satellite and aerial images with greater speed, accuracy and insight.

Transmission Electron Microscope (TEM)

In TEM, as a beam of electrons is transmitted through an extremely thin specimen, an image of the specimen is formed and magnified. This image appears on a screen. It can also be directed to appear on a layer of photographic film or detected by a sensor. It is an imaging technique.

The scope of TEM can be extended by incorporating additional stages and detectors on the same microscope. A TEM can also be modified as a **Scanning Transmission Electron Microscope or STEM.**

TEM is a valuable tool for research in materials science, biological science and nanoscience as TEM gives very high magnifications of samples. We can get a resolution of 1 Å and can see very small objects (< 1 nm).

Specimens for TEM must be very thin and able to withstand the high vacuum present inside the instrument. The thickness of biological specimens must not exceed 1micrometre. Biological specimens are typically kept at liquid nitrogen temperature to withstand the vacuum in the microscope.

Disadvantages of TEM: This technique requires extremely thin and electron transparent samples. Therefore, as sample preparation requires time TEM analysis can be a time-consuming process. During the preparation of the sample, the structure of the sample may change occasionally. There is also the possibility of the sample being damaged by the electron beam.

How does TEM work?

The transmission electron microscope works on the same basic principles as the light microscope. However, TEM uses electrons instead of light. There is a phosphor screen at the bottom of the microscope.

The magnification possible with a light microscope is limited by the wavelength of light. As the TEM uses electrons as "light source", the much lower wavelength of the electrons gives high resolutions and makes it

possible to see materials at atomic or cellular levels. Also, the TEM uses electromagnetic lenses to focus the electrons into a thin beam.

The electrons emitted by the electron source at the top of the microscope travel through the vacuum in the column of the microscope. The electromagnetic lenses guide the electrons and the electron beam travels through the sample. Some of the electrons of the electron beam are scattered. The unscattered electrons pass through the sample and hit a fluorescent screen at the bottom of the microscope, giving a "shadow image" of the specimen.

The different parts of the sample are displayed in varied darkness according to the density of electrons. The image can be studied directly or photographed with a camera.

Scanning Electron Microscope (SEM)

Scanning electron microscopy is a friendly way of doing microscopy with high magnification. In SEM, a monoenergetic electron beam is focused to a point on the sample surface through pairs of scanning coils in the objective lens. The beam is deflected horizontally and vertically so that it scans in a raster fashion over a selected rectangular area of the sample surface. Secondary electrons emerge

from the illuminated area and they carry the information on

the topography of the surface. The brightness of the signal depends upon the number of secondary electrons reaching the detector. The difference in signal intensity from different locations on the specimen allows an image to be formed.

SEM has a large depth of field. This allows a large amount of the sample to be in focus at one time. Also, the data collection may be restricted to small regions thereby increasing the resolution up to 1 nm. The samples need to be conductive. To view non-conductive samples such as ceramics or plastics, we must cover the sample with a thin layer of a conductive material. We can see objects of ~ 20 nm or so in most SEM instruments. SEM is particularly useful to characterize soild materials. SEM is user friendly.

Many specializations are possible with a working SEM column. X-rays which are produced by the interaction of electrons with the sample may be detected in a SEM equipped for energy dispersive X-ray spectroscopy. Elemental composition can be obtained using this method.

Scanning Tunnelling Microscope (STM)

A scanning tunnelling microscope provides three-dimensional atomic-scale images of the surface of a sample. STM has a stylus with an extremely sharp tip. The stylus scans the surface of the sample from a fixed distance. STM is used to study the structure of the surface of the sample.

The stylus is raised and lowered so that the distance of the stylus from the sample is maintained and the signal is kept constant. The stylus scans the surface of the sample slowly from a distance of only the diameter of an atom. This allows

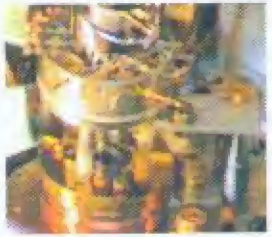
the stylus to scan even the smallest details of the surface of the sample and build a three-dimensional profile of the surface.

STM is a powerful tool for viewing surfaces at the atomic level. STM is very versatile as it can be used in ultra high vacuum, in air and various other liquid or gas ambients and at temperatures ranging from near 0 Kelvins to a few hundred degrees Celsius.

The concept of **'quantum tunnelling'** forms the basis of STM. When the conducting tip of the STM is brought very close to a metallic or semiconducting surface of the sample, a bias or voltage difference applied between the conducting tip and the sample surface allows electrons to tunnel through the vacuum between them.

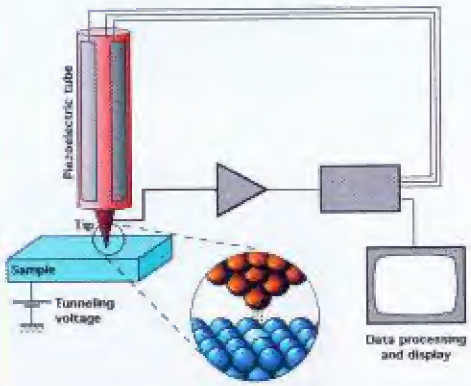
STM requires very sharp stylus tip and an extremely clean sample surface. STM uses a sharp metal wire, usually of tungsten or a Pt-Ir alloy, as the probe. The tip is prepared either by using a mechanical cutter (Pt-Ir tip) or by electrochemically etching away the metal (tungsten

tip). Both can be done in the laboratory. **The tip essentially consists of a single atom.**

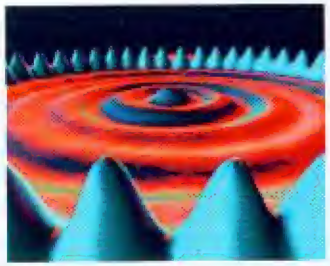


STM requires a vibration-free environment. To prevent vibrations, it has airlegs or mechanical or gas spring system and a big steel platform. In the STM set up used here, the tip is hanging from a piezo-tripod. The three piezo legs control the tip motion within a fraction of an Angstrom. This set up allows us to do STM under high vacuum and also at low temperatures.

How does STM work?

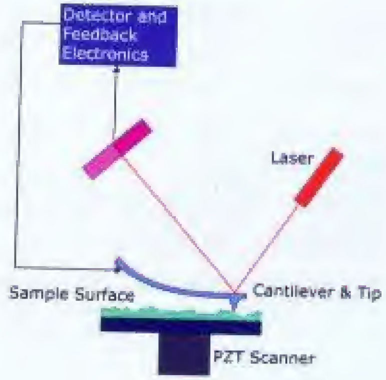


As the tip is made to move over the surface of the sample, at close quarters to the surface, its electrons tunnel between the surface of the sample and the tip (i.e. the small bias between the surface and the tip makes tiny electrical current to flow through due to quantum tunnelling).



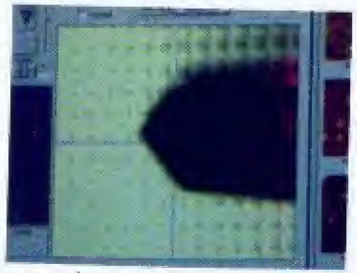
A contour of the surface is obtained. The detailed cross-sectional image at the atomic scale so obtained helps to move atoms and molecules around. Researchers at IBM created a quantum corral of 48 iron atoms by placing them in the shape of a corral.

Atomic Force Microscope (AFM)



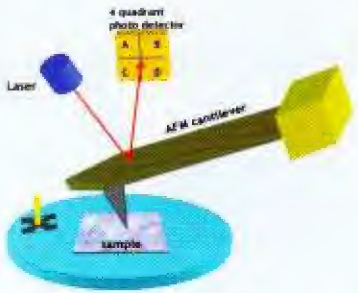
A typical AFM has a microfabricated cantilever with a sharp tip. This tip is deflected by features on a sample surface. A laser beam reflects the deflections off the backside of the cantilever into a quadrant of photodetectors. Using these data, deflections can be measured and an image of the surface can be assembled.

AFM was invented to study biological samples as STM could work only in vacuum. AFM measures the force between atoms. A hard tip, usually made of silicon nitride, mounted as an inverted pyramid on a cantilever arm forms the probe. The radius of curvature of the tip is only a few nanometers (one or two nanometers). The sharp tip scans the sample point by point.



To avoid air-borne or mechanical disturbances in this delicate instrument, the microscope as a whole is mounted in a hood on a vibration-free platform. The AFM tip cantilever is mounted on a piezo-driver tube. This allows one to control the tip motion to approach a surface and scan a region of interest. A small voltage can bring about nanometric

distortion in the tube geometry. This property has been exploited to make it work as a tip scanner.



The scanner assembly is placed in a box which also houses a pointed laser and a position sensitive detector. The laser beam shines on the backside of the cantilever and the reflected beam is picked by the detector. Any tip motion, however tiny, is sensed. A part of the signal is fed to a feedback circuit to guide and control the sensitivity of the scanner.

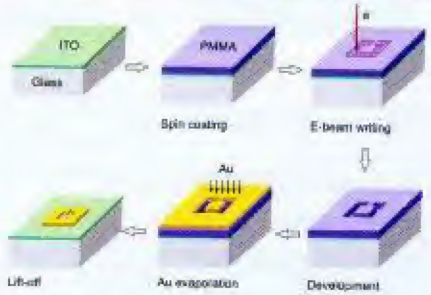
How does AFM work?

The working of AFM is based on measuring the force between atoms. The tip is brought close enough to the surface under examination for the tip to start feeling the local attractive and repulsive forces.

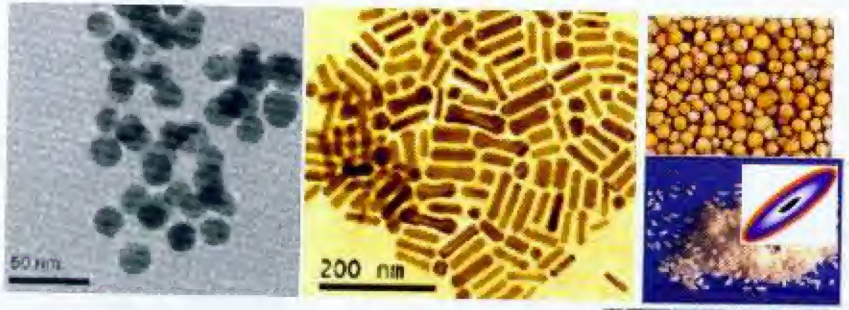
Once the tip interaction with the surface is sensed from tiny vertical displacements, it is made to move in a raster fashion across a selected area (say 1000 nm by 1000 nm). The vertical displacements at each point is recorded and displayed on a computer screen as a 3-D image using a color code (higher the displacement, brighter is the color). In this way, the topography of the surface being scanned is obtained. Another advantage is that AFM can provide real time images of a sample in a liquid state. To obtain the best images of the sample it is essential that no other disturbance or noise adds to the tip motion. AFM tip is used as 'pen' in dip pen lithography or DPN.

Generating patterns on electron sensitive materials

Using the electron beam from the SEM column, one can generate patterns on electron sensitive materials. **This technique is known as electron beam lithography (EBL).** Generally, polymers (e.g., poly (methyl methacrylate) PMMA) are used as e-resists. **Electron beam-induced deposition (EBID)** is a process in which a gaseous metallo-organic precursor is introduced in the chamber, in close proximity to a substrate surface and electron beam is employed to decompose it. Volatile by-products are released leaving behind the metal patterns. Both methods are highly useful in nanocircuit fabrication.



9.0 Preparation of nanomaterials



A nanoparticle may be spherical. It may also be a rod or a cylinder. We can have spherical particles shaped like mustard seeds or particles shaped like rice grains.

We can prepare metals, semiconductors, oxides and a variety of materials in the form of nanocrystals of different shapes, or as nanowires and nanotubes. We can also make them in the form of nanofilms.

Au Bi - pyramids

Different methods of preparing nanomaterials

There are physical as well as chemical methods to prepare nanomaterials.

Physical methods: We can grind materials using ballmills or evaporate materials to the gas phase to obtain small particles. We can also use lasers to produce small particles.

The most powerful methods, however, are the chemical methods.

We can react a metal salt with an alcohol or some other reducing agent (like citric acid) to prepare nanoparticles of metals. Such small metal particles dissolve in certain organic solvents and form solutions.

In order to prepare nanoparticles of metals, oxides and such materials, one can take a metal compound along with a reagent in a boiling solvent (water, hydrocarbon or organic amine) and heat it. It is often preferable to heat it in a sealed vessel that acts as a **"bomb"**. Under these conditions, many kinds of nanoparticles are formed.

Hydrothermal and solvothermal methods

When water is used as the boiling solvent, the method is called

the **hydrothermal method**. When a boiling organic solvent like a hydrocarbon is used, it is called the **solvothermal method**. For example, if we take a metal acetate and heat in a bomb in a hydrocarbon solvent, we get metal or metal oxide nanoparticles.

Solvothermal reactions

Solvothermal reactions are popular for the synthesis of various kinds of nanomaterials. One often adds a polymer or a capping agent to the reaction mixture to control the shape and size of particles. After synthesizing the particles, one can also carry out selective crystallization to get particles of the same size.

The main point to note is that today we have reached a level where we can make nanomaterials of any compound in any shape we desire.

Inorganic nanotubes

Carbon nanotubes have been known since 1991. Few years later, it was possible to make nanotubes of metal sulfides, metal

MoS_2 nanotubes

BN nanotubes

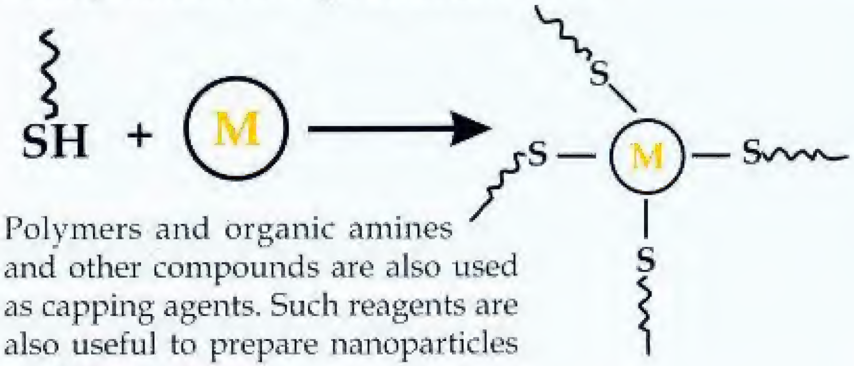
TiO_2 nanotubes

oxides and other materials. Nanotubes, therefore, need not be of carbon alone.

Assembling nanomaterials

After making the nanomaterials, how to put them together in an organized manner for applications is another challenge. Various kinds of chemical reagents are used to make assemblies of nanostructures.

In the case of metal particles, alkane thiols which contain the S-H bond are commonly used. The thiols attach themselves to metal particles forming metal-sulfur bonds.

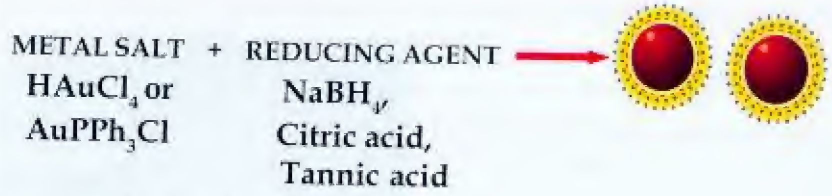


Polymers and organic amines and other compounds are also used as capping agents. Such reagents are also useful to prepare nanoparticles of different shapes.

Preparation of metal nanoparticles

Nanoparticles of metals (such as gold) are usually made by reducing metal salts in some solvent using an appropriate reducing agent. A typical reducing agent could be **citric acid or a metal hydride.** The reduction is sometimes carried out in the presence of polymers or some other chemicals in order to control the size and shape of the particles.

Solutions of Au nanoparticles of different sizes



Preparation of graphene

Single layer graphene is produced by peeling off the top layer of graphite by a scotch tape. The layer is then put on a solid support to study the properties. By sonicating graphite vigorously in water or some other liquid, graphene layers get dispersed. Chemical methods are also known. Methane can be decomposed on the surface of a metal such as nickel to get graphene. Another method is to prepare graphitic oxide by oxidation of graphite and obtain single layers of graphene oxide by thermal shock. The single layers of graphene oxide are then reduced to obtain graphene.

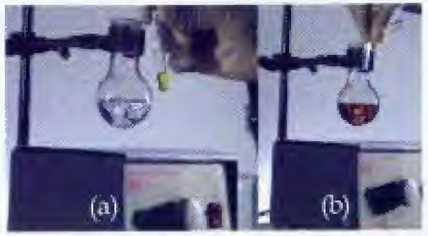
Experiments on gold nanoparticles and zinc oxide nanowires

Let us see how we can make nanoparticles of gold.

Take ~23.5 ml of 6.38 mM NaOH solution in a round bottom flask containing a magnetic pellet and stir the solution. (We have to add PVA, a polymer to control the size of the particles). Using a micropipette add ~0.5 ml of a freshly prepared 50 mM solution of THPC [tetrakis (hydroxymethyl) phosphonium chloride]. This is used as a reducing agent. Note that the solution is **colorless** (see (a)).

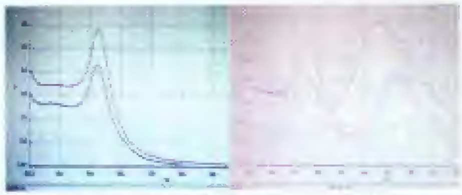
Now, slowly add 1 ml of aqueous solution of chloroauric acid, $HAuCl_4$, a gold compound. What do you observe? The color

changes immediately. The solution containing chloroauric acid becomes pale brown (see (b)). The color is due to the formation of nanocrystals of gold. The nanoparticles of Au thus formed are very small in size.



How can we know the size of the gold nanoparticles that we have made?

Gold nanoparticles have different colors depending on their size. The color comes because the electrons in the nanoparticles of gold get collectively excited by light. Instead of saying that the color is yellow, brown or red, we can take a spectrum of the solution of gold nanoparticles. We will take the spectrum using this spectrometer. In this spectrometer, the light we use is UV or visible radiation. The spectrum gives the wave length at which these particles absorb light. We see a band at 520 nm (5200Å) due to the excitation of



Spectra of gold nanoparticles

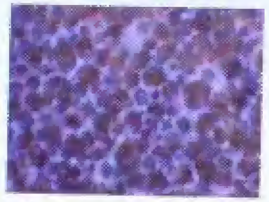
electrons in Au particles. The spectrum changes with the size and shape of the particles.

Determining the size of the gold nanoparticles using an electron microscope

Take a drop of the solution containing gold nanoparticles. Place it on a grid in a transmission electron microscope. Look at the

Preparing the sample for determining the size of the gold nanoparticles using TEM

gold nanoparticles in this microscope and take an image. The nanoparticles have sizes between 2 and 4 nm. We have conducted a simple experiment to prepare gold nanoparticles and characterize them by simple techniques using an electron microscope and a spectrometer.



TEM image of gold nanoparticles

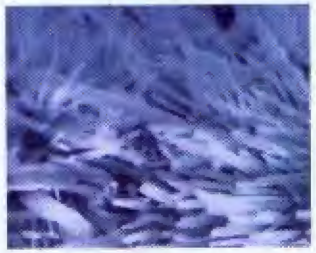
Let us prepare nanowires of zinc oxide (ZnO)

Take 50 -100 mg of zinc metal powder in a sample vial. Add 5 ml of water to it. Add 1-2 ml of ethylene diamine to the solution in the vial using a dropper.

Using the Scanning Electron Microscope (SEM) take images of the zinc metal powder. Keep the sample vial containing the zinc solution for a week at room temperature.

SEM images of zinc oxide nanowires

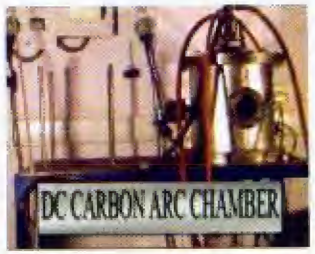
Remove the solvent from the vial. Dry the sample under vacuum. Redisperse the dry sample in carbon tetrachloride. Use a dropper and load the sample on a sample holder and place it inside the Scanning Electron Microscope. The images show nanorods or nanowires with diameter in 20-80 nm range. This is a simple preparation but all nanowires cannot be prepared so easily. Many are prepared using complex chemical methods.



Preparation of carbon nanotubes and copper sulfide nano films

Let us make some carbon nanotubes by the arc discharge method.

As mentioned earlier, the discovery of carbon nanotubes was first made in 1991. They were made by having an electric discharge between two carbon electrodes. The material that was collected at the cathode had nanotubes. This is an arc discharge chamber. It operates at 30 volts DC and 60 amperes.



There are two carbon electrodes. The anode is

a 6 mm graphite rod which will be consumed during the DC arc discharge process.

Procedure: Place the top lid containing the cathode inside the chamber. Strike an arc by using electricity (30 DC and 60 amperes). The temperature in the chamber rises to ~4000^{0}C. During this process, the graphite anode gets evaporated and is deposited on the cathode as black soot. Cool the chamber containing the electrodes with cold water. Collect the cathodic deposit.

TEM images of carbon nanotubes

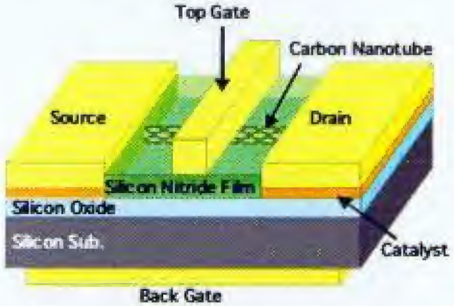
Scoop a portion of the cathodic deposit into an agate mortar. Add a few ml of CCl_4 solvent and grind the sample using a pestle.

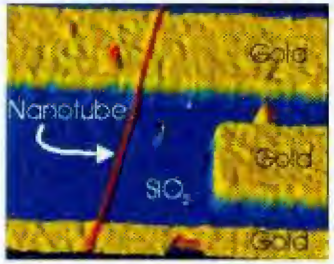
Add a drop of this suspension to a Transmission Electron Microscope (TEM) grid and dry it.

10.0 From nanoscience to nano technology

What is nanotechnology?

Nanotechnology involves the use of nanomaterials in various areas such as chemical and textiles industries, biotechnology, electronics and medicine.





Carbon nanotube transistor

It is also a technology used to fabricate devices in the 1 to 100 nm range. Simply put, nanotechnology is the application of nanoscience to control matter within a size range of 1 to 100 nanometers and involves the fabrication of various devices within that scale.

Eric Drexler (1955-)

Eric Drexler is famous for popularising the unlimited scope of nanotechnology to fabricate molecular nanodevices. Drexler was greatly influenced by the book "Limits of Growth" published in 1972 which outlines the consequences

of a rapidly growing world population on the finite amount of resources available.

Drexler believed that it was possible to build **"molecular assemblers"** - nanodevices which were capable of placing **"atoms and molecules as required for any precisely defined reaction in almost any environment"**. In his famous book "Engines of Creation: The Coming Era of Nanotechnology" published in 1986, Drexler described a world completely transformed by molecular assemblers. He was convinced that they would be able to build anything with absolute precision and no pollution. They would even enable the colonization of the solar system. Drexler was also aware that these "assemblers" would pose serious threats to life on Earth.

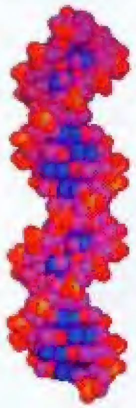
He coined the word **"Grey goo"** a hypothetical situation in which out-of-control molecular assemblers replicating themselves would consume all living matter on Earth. He, therefore, urged that the society must thoroughly understand both the creative and the destructive scope of these assemblers and make sure to develop safety mechanisms to ensure only the beneficial applications. However, Drexler's prophecy of molecular assemblers becoming a reality has not found acceptance.

Nanoelectronics covers all aspects of electronic devices and technologies (including computers) that make use of nanomaterials. Note that transistors have been made using carbon nanotubes and inorganic nanowires.

Seidel *et al.* Nanoletters 2005

11.0 Nanobiotechnology

Nanobiotechnology as the name suggests is the fusion of nanotechnology and biotechnology. It is a fairly new area of research and technological opportunity. There are innumerable examples of nanoscale processes and structures that govern biosystems. The living cell has hundreds of nanomachines powering its multiple functions. It represents highly precise nanoscale fabrication. Researchers use the knowledge gained by molecular biology in studying molecules in the range of nanometers (DNA and proteins for example) to create new micro/nanoscale devices to understand life processes at the nanoscale more comprehensively.



Nanobiotechnology is an interdisciplinary area where there is close collaboration between life scientists, physical scientists, and engineers. The inspiration and ideas for specifically fabricated nanodevices to analyse specific biological systems come from bio-structured molecular machines. In the molecular machines of the living systems, biomolecules are used as building blocks and biosystems as fabrication machinery.

Here again, two approaches are possible to fabricate nanodevices- the top-down approach and the bottom-up approach. Nanodevices in biological systems use the bottom-up approach using atoms and molecules as building blocks

to fabricate systems in living organisms. The advantage of the bottom-up approach is that the covalent bonds binding atoms in a molecule are stronger than the intermolecular force. A field where nanobiotechnology has been put to use is in the development of nanomedicine. The term **nanomedicine** is generally used to cover all those aspects of nanoscience and technology employed in health care related areas including tissue engineering, gene delivery, drug delivery, biomedical sensors and so on.

New methods have been developed to monitor diseases by implanting a semiconductor chip inside the patient's body to monitor the medical parameters. The acquired data are transmitted to a device worn by the patient. The device analyses the data and instructs the chip to act as the drug delivery system to deliver the right amount of medicine.

12.0 Molecular motors

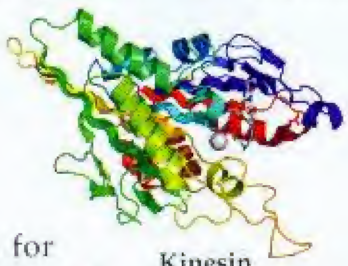
The challenge of fabricating man-made molecular motors was first mooted by Richard Feynman of the California Institute of Technology in his talk **'There is Plenty of Room at the Bottom'**. Ironically, even as he threw his challenge, he was not aware that there were already countless devices far smaller and more powerful than he imagined functioning inside the human body. In fact these devices have been functioning in nature for millions of years. Countless molecular motors are working within every cell of living organisms. Some of these motors

are thousands of times smaller and more efficient than any device we have built till now.

A molecular motor is an assembly of a finite number of molecular components which performs mechanical movement when subjected to external stimulus. The molecular motors have integrated multiple structures and processes. They are also organized to mutually support each other and at the same time support various functions of the motor.

Molecular motor generally refers to proteins found in living organisms which consume chemical energy and transform it to mechanical energy (movement, transportation within the cells). Cells in our body abound in molecular motors. Different motor proteins in our body perform different specialized tasks in the human cells. Myosin (responsible for muscle contraction), kinesin (responsible for movement of 'cargo' inside the cell) and ATP (responsible for providing chemical energy) are some of the important motor proteins. There are two kinds of biochemical molecular motors. They are linear molecular motors and rotary molecular motors. The molecular motor that rotates a flagellum is an example of rotary motors.

Myosin



Kinesin

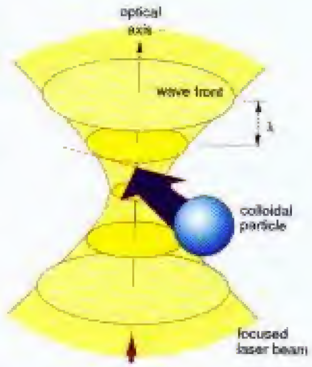
Naturally occurring biological molecular motors have inspired nano scientists and nanotechnologists to fabricate nanomotors to do a variety of tasks both within the human body and outside it. Until recently the term molecular motor referred to

naturally occurring proteins in living organisms that use chemical energy to induce a variety of motions. Many nano scientists and technologists now routinely use the term to refer to non-biological and non-protein based motors fabricated by them. Molecular motors unidirectional as well as repetitive 360° motion and consumption of energy to produce this motion are fabricated using new technology. Scientists are working on chemically driven motors as well as light driven motors.

Molecular motors using chemistry have been designed. These use specially designed molecules which act like wheels and gears. A motor has also been made by employing the decomposition of hydrogen peroxide as the source to generate translational motion.

13.0 Optical Tweezers

An optical tweezer is a device that uses light to move around and manipulate nanosized particles as well as even single atoms. In an optical tweezer, a tightly focused laser beam is passed through a high power microscope objective as lens to a selected tiny spot in the plane of specimen. An optical trap is created at that spot by the focused laser beam. The trap is capable of holding extremely small objects between 10 nm and 100 micrometers in size.



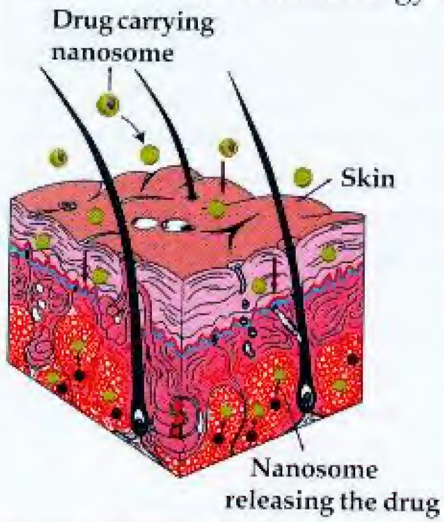
How does an optical tweezer create the trap? The light of the laser beam is not uniform throughout the beam as it is tightly focused. It is less intense or bright around the edges of the beam than at its centre. When the light from the laser beam strikes the particle of the specimen, the light rays undergo reflection and refraction. This change of direction in the path of the light results in a change of momentum of the light. The particle feels the two components of the light's forces - the scattering force and the gradient force. These forces create a small optical trap capable of holding a very small particle of nanometric size at its centre and the specimen particle is trapped there. Optical tweezers can move the trapped nanoparticles around and manipulate them in the desired manner.

Optical tweezers are useful to study not only biological systems but also to manipulate nanoparticles. They have been extensively used to study and characterize the functions of motor proteins and the physical properties of DNA. Optical tweezers enable scientists to actually see nanosized objects. It is becoming an invaluable tool to study the nanoworld. Optical tweezers are no longer the simple tools used to manipulate objects of few micron in size. They are now very sophisticated computerized devices that are capable of trapping nanoparticles and measuring even the tiniest displacement and capable of giving a circular motion to the motors.

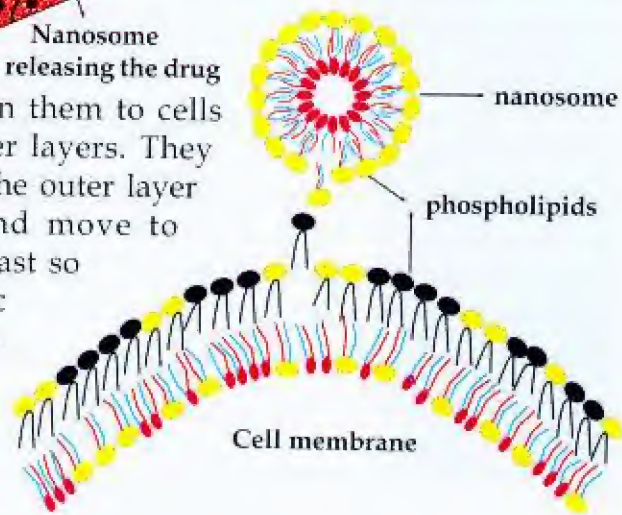
14.0 Applications

14.1 Nanocosmetics

Nanotechnology has revolutionized cosmetics industry and helped it to take an altogether new path. Cosmetic industry has harnessed the technology to use nanoparticles (patented by one cosmetic giant as nanosomes) as delivery systems.



Nanosomes are nanoparticles ~800 times smaller than human hair. They are like carrier or delivery bags. These particles can penetrate the outer layer of the skin and deliver the nutrient materials encapsulated in them to cells below the outer layers. They can penetrate the outer layer of the skin and move to deeper layers fast so that cosmetic formulations are effectively absorbed and new cells are produced.



Production of new cells helps the skin to remain soft and wrinkle free regardless of age. Nanoparticles as a delivery system perform another important function. They also help to eliminate waste products from the cells.

Nanoparticles are also being used in cosmetic industry to broaden the range of chemicals like vitamins and growth promoters that can be safely used as supplements in skin revitalising and anti-aging formulations. The outer surfaces of these chemicals are coated with nanoparticles to prevent irritation in the stomach if taken in their raw form. The nanoparticles cross through the stomach walls effectively, enter into the blood stream and deliver the chemicals and nutrients to cells. The nanoparticle coating protects the encapsulated contents from degradation until delivery to their final target. They merely aim to create an appropriate nutrient rich environment for cells to remain healthy and wrinkle free. However, nanoparticles used in cosmetic skin formulations have no medicinal value or curative properties and cannot be used to rejuvenate unhealthy skin.

With a majority of women and men wanting to look young and fair (at least in India), the cosmetics market is expanding by ~ 10% a year. Cosmetic companies are convinced that nanotechnology will help to create a new generation of cosmetic products. They are also looking forward to finding through the nanocosmetics route hair care formulations soon to prevent greying and loss of hair or even baldness.

While research into the use of nanoparticles and nanotechnology to prepare newer skin and hair rejuvenation products is a profitable investment for cosmetic industry, serious concerns are being voiced about the long term effect of these products on the overall health of the users. As

mentioned earlier, skin care products using nanoparticles penetrate cell walls to deliver their cargo. This poses many questions about their toxicity effects.

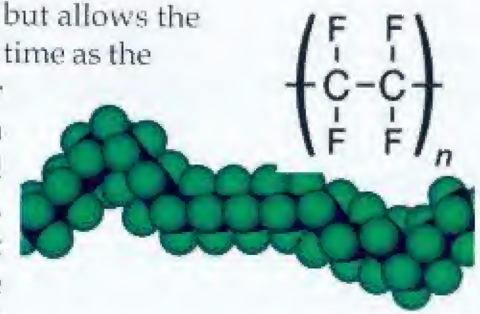
14.2 Textiles

What is common between lotus leaves and nanotextiles?

Water droplets skid off both lotus leaves and nanotextiles. Water droplets just skid off lotus leaves because they have superhydrophobic surface as the surface of the leaves are coated with hydrophobic wax nanocrystals which repel water droplets and minute dust particles. Mimicking this, textile scientists have produced stain and wrinkle proof textile material by coating the fabric with a thin layer of extremely hydrophobic silicone nanofilaments. The unique spiky structure of the filaments creates a 100% water proof coating. Water droplets rest on the silicone coating and slide off the cloth when the garment is just tilted. In addition to water proofing the material, silicone filaments create a permanent layer of air by trapping air between the layers of the nanofilaments. This trapped layer of air prevents moisture from seeping through and making the garment wet.

Porous **Polytetrafluoroethylene or PTFE** is used to manufacture clothing that protects the wearer from

rain, wind and even snow but allows the skin to breathe at the same time as the coating allows water vapour to pass through but does not allow liquid water to pass through. PTFE treated fabrics act like nanofilters - the protective inner layer protects the fabric from stains from body's sweat and oil and the outer layer protects the fabric from damage.



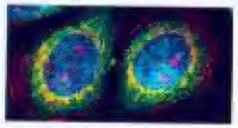
Antibacterial and antifungal properties of silver nanoparticles are used to produce a range of clothing impregnated with silver nanoparticles. Socks made of such material are useful in inhibiting the growth of bacteria and fungi which cause toe nail infections, foot odor, and painful cracks in the heel. Use of silver nanoparticles is based on the antibacterial and antifungal properties of silver nanoparticles.

14.3 Nanosensors

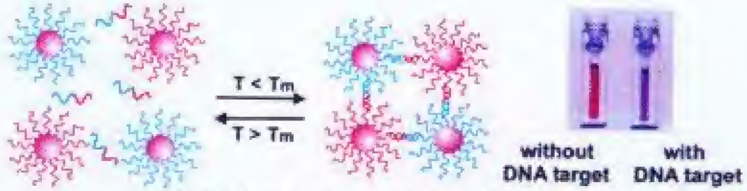
Sensors are used in a variety of ways in daily life. Sensors are used in traffic lights to ensure smooth flow of traffic, to open doors at malls and airports, to detect smoke or fire in hotel rooms etc. These are not nanosensors. Nanosensors which act as receptors of external stimulations are found in the animal and plant world. For example, dogs are able to detect smell by using receptors that are sensitive to nanosized chemical molecules. Certain types of fish have nanosensors that can detect minute vibrations in water. Nanosensors are devices that use biological, chemical or mechanical sensory points to

detect and convey the information about the nanoregime under investigation. Use of nanosensors have great potential in the world of medicine (to accurately identify specific cells and their location and distinguish between healthy cells and cells affected by disease) and in the physical world as well. Nanosensors can be used to detect harmful gases. Nanosensors used in medicine are programmed to measure changes in the concentration of fluids, changes in volume, electrical and magnetic forces as well as pressure and temperature of cells in a body.

Biological nanosensors have been used to explore the mysteries of the living cell. Using nanotechnology, it is possible to build nanodevices capable of manipulating molecules in a living cell by combining advances in biology, advanced materials and photonics. Using the nano-scale sensors, it is possible to make various measurements in the micro-environment of an individual cell. Changes in the colour of semiconductor nanocrystals (e.g. cadmium selenide or gold nanoparticles) are exploited in certain applications.



Study of cells using CdSe nanoparticles
Source: Mednitz *et al. Nat. Mater.* (2005)

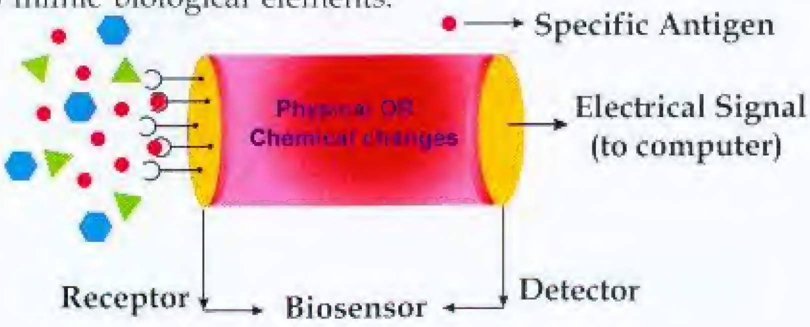


DNA sensing using Au Nanocrystals
Source: Mirkin & Rosi, *Chem. Rev.*, 2005

Chemical sensors basically work by monitoring changes in the electrical properties of the nanotubes or inorganic

nanostructures used as sensor materials. The nanotubes/ nanostructures are coated with a material which makes the sensor sensitive only to a specific material and immune to other materials present in the surrounding environment. Using carbon nanotubes, chemical nanosensors have been fabricated to detect glucose while ZnO nanotubes have been used to measure concentration levels of hydrogen or ethanol. These sensors act specifically with a molecule. Chemical sensors have been fabricated to detect different gas molecules.

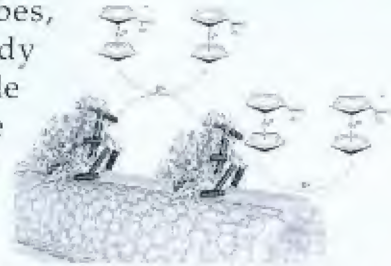
Biosensors: A biosensor has the following components: a) A biological sensing element or material which can be natural biological elements such as microorganisms, cell receptors, enzymes, nucleic acids, antibodies, or biomaterials designed to mimic biological elements.



b) A detector element or transducer. It measures and converts detectable physicochemical changes that occur when the biological material interacts with the analyte into electrical signals. c) Signal processors or electronic devices. These components of a biosensor have specific functions. The key functions performed by the biological component of the biosensor are to recognize the analyte and to interact with it to produce some detectable physicochemical change.

Biosensors convert chemical information into electrical information in a series of steps. First the analyte reaches the surface of the biosensor device by diffusion. It then reacts with the biological component of the device. The reaction changes the physical and chemical properties of the surface of the transducer leading to changes in optical or electronic properties. These changes are converted into electrical signals.

Using carbon nanotubes, scientists have already developed tiny implantable biosensors to detect glucose levels continuously. Carbon nanotubes sensors wrapped with DNA are useful to monitor anticancer drugs and ensure that the administered drugs are indeed fighting the disease.

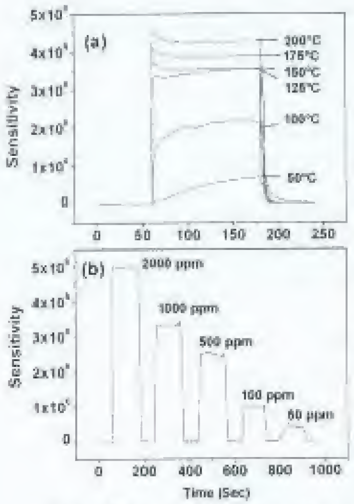


A SWNT glucose biosensor

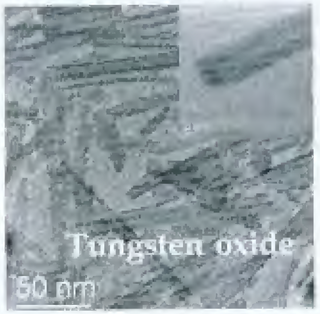
Source: J.J. Davis et al., *Chem. Eur. J.* 2003

Gas sensors: A gas sensor is a device that detects the presence of a gas present even in traces in the vicinity of a given location.

It interacts with a specific gas and measures its concentration. The gas flows over the sensor to produce an electrical signal. The sensor is non-biological. Gas sensors are generally used in industries for process control, for monitoring environmental pollution, for sensing smoke to detect fire and traces of LPG leak, to measure the level of alcohol in the blood (breathalyser test) and for detecting traces of dangerous gases in mines and in industries.



Hydrocarbon sensor based on WO_3



Various technologies are used to make gas sensors. The most commonly used gas sensors are metal oxide based gas sensors (These sensors are also known as Chemiresistors), capacitance gas sensors, acoustic wave based sensors, calorimetric gas sensors, optical gas sensors, and electrochemical gas sensors.

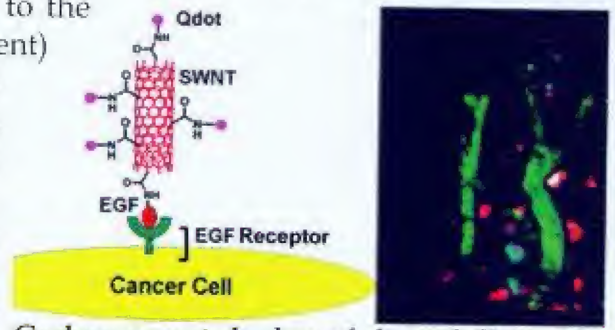
Some of the important gases detected by oxide gas sensors are hydrogen, ethanol, hydrogen sulphide, nitric oxide, ammonia and hydrocarbons.

Mechanical sensors: These are also based on the principle of measuring the electrical changes just as chemical sensors. For

example, sensors used in airbags in cars measure the changes in the capacitance.

14.4 Drug Delivery

Two major problems with drug delivery systems used till now are how to ensure the presence of the molecules of the administered drug where they are needed (or where they are most beneficial to the body of the patient) and an effective biodistribution of the drug in the body. Therefore, one of the major thrust areas of nanomedicine is to develop drug delivery systems using nanotechnology and nano-engineering to overcome these two roadblocks. Nanomedicine has approached the problem by developing suitable nanoparticles or molecules of biocompatible materials to increase the bioviability to the maximum for the longest period possible at specific sites in the body.

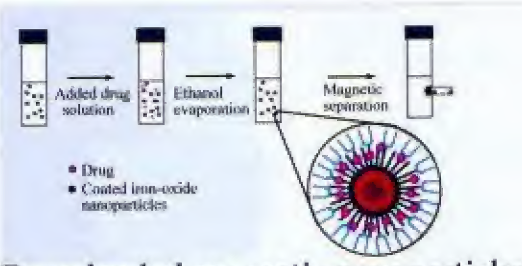


Carbon nanotube based drug delivery for targeted killing of cancer cells

Source: Ashwin A. Bhirde et al., *ACS Nano*, 2009

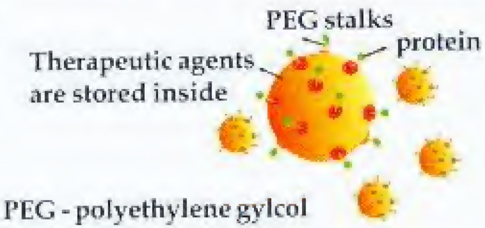
However, to develop efficient drug delivery systems using nanomaterials, several factors such as the interaction between the nanomaterial with the biological environment and the targeted cell surface receptors, method of drug release, pathobiology of the disease under treatment, molecular

mechanisms of cell to the administered drug have to be well understood. The efficiency of the drug delivery system, therefore, depends upon the efficient encapsulation of the drug molecules, delivery of the drug to the selected site with precision and successful liberation, absorption and the distribution of the drug. Consequent metabolic activity and excretion of the metabolites harmful to the body are also important for the success of the drug delivery system.

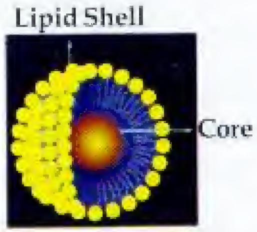


Drug-loaded magnetic nanoparticles

Using the special properties of nanoparticles, improved drug delivery systems are being developed by improving the biodistribution and altering the pharmacokinetics (the action of the drug over a period of time) of the drug where necessary. Improved drug delivery systems have the ability to get the drugs through cell membranes and into the cell cytoplasm. Whereas larger particles of the drug molecules are generally not accepted by the cells, they accept nanoparticles because of their tiny size. Nanoparticles are used as tags to deliver the drug across the



Nanoparticle built with biocompatible material



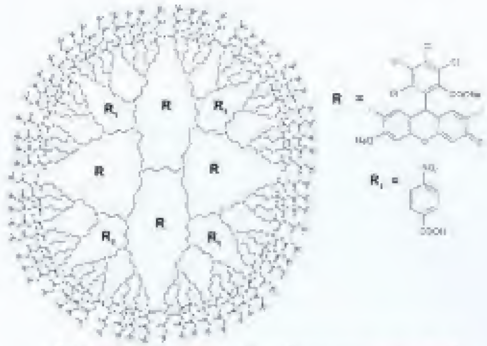
The core contains therapeutic agents

barrier. This delivery system is a great boon as many life threatening diseases are dependent on the processes taking place within the cells. It can also deliver large macromolecule drugs to intercellular sites where they are required to fight the disease.

Drug delivery can be an injectable drug delivery system or an implantable drug delivery system where the molecule of the drug is implanted in the body. It can also be a delivery system where the nanoparticles of the drug molecule enter the tissues and cells of the targeted location. It can also be a transdermal system with more effective diffusion of drug molecules through the dermal tissues. However, the most preferred delivery system, is the oral drug delivery system.

Nanoparticles of the drug are found to be useful in treating brain disorders as they have shown the ability to cross the brain blood barrier (BBB) without the need either to open the brain or to modify the drug (which may reduce its efficacy). Some researchers have used nanospheres derived from hydrogels as carriers. These hydrogels are extremely stable organic compounds that swell when the environment inside the body becomes increasingly acidic (e.g. the environment in the stomach).

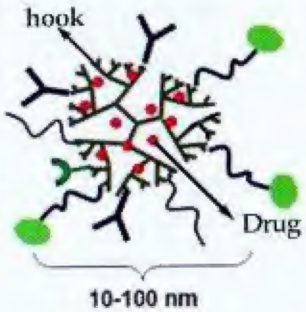
An interesting type of molecule for designing a delivery system is an organic dendrimer, a special

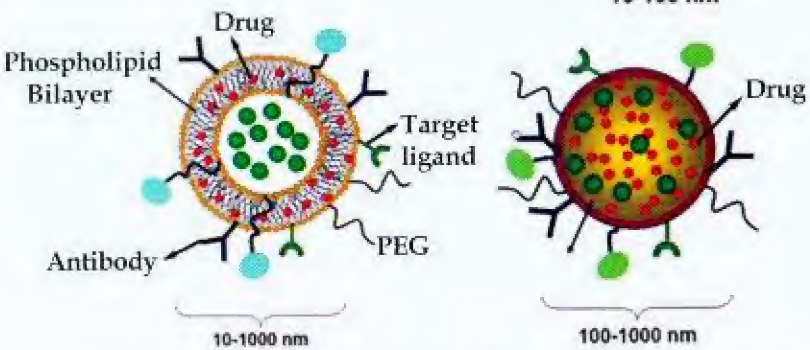


Dendrimers in drug research

Source: Ulrik Boas & Peter M. H. Heegaard, *Chem. Soc. Rev.*, 2004

class of spherical polymer molecules. A dendrimer molecule can move in and out of a central region of the molecule. This molecule has more than hundred hooks on it. The hooks enable the molecule to attach itself to cells in the body. The effectiveness of drugs can also be improved many folds by using lipid or polymer based nanoparticles to design drug delivery systems.





Lipid and polymer based nanoparticles

Source: Tarek M. Fahmy et al., *The AAPS Journal 2007, 9(2) Article 19*

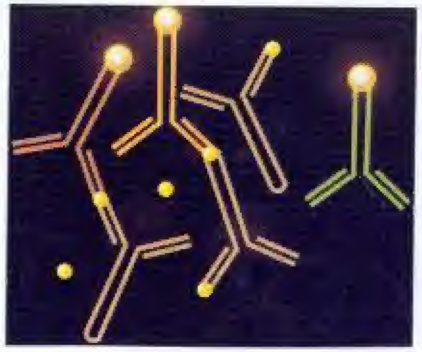
14.5 Cancer Therapy

Nanoscience and technology is expected to have a major impact on cancer treatment by developing drugs with nanosized molecules with more targeted efficiency and less side effects and toxicity. Major problems with cancer treatment being used (chemotherapy and radiation therapy) are that the drugs are released in more than required quantities and are not area-specific. In addition to causing severe toxicity it results in extensive collateral damage to surrounding tissues. Size-

dependent properties of nanoparticles can be used both for imaging and developing more efficient drug delivery systems in treatment of cancer. Fluorescent quantum dots have size-dependent light emission property and need only one light source for excitation. They can produce images of exceptional clarity of the tumor site at lower cost when they are used as contrast media in conjunction with magnetic resonance imaging or MRI. When cadmium selenide quantum dots are injected, they seep into cancer tumors. When ultra violet light is shone on the area, cadmium selenide quantum dots glow. Surgeons can use this to locate the site of the tumor accurately and remove it with minimal damage to the surrounding tissues.

Selective targeting and killing of cancer cells via receptor binding and NIR laser radiation

The high aspect ratio of nanoparticles can be harnessed to attach the required functional group which can seek out and bind themselves to certain tumor cells.



Fluorescent tags for detection of cancer-associated proteins

Another drug delivery system that may one day replace chemotherapy is the **Kanzius RF therapy**. In this therapy, gold nanoparticles are attached to cancer cells and are subjected to radio waves. As the metal absorbs the energy from the radio waves more efficiently than living tissue, the gold nanoparticles get heated faster and more efficiently by dielectric heating and the cancer cells are 'cooked' inside the body and killed while the healthy cells are left unaffected.

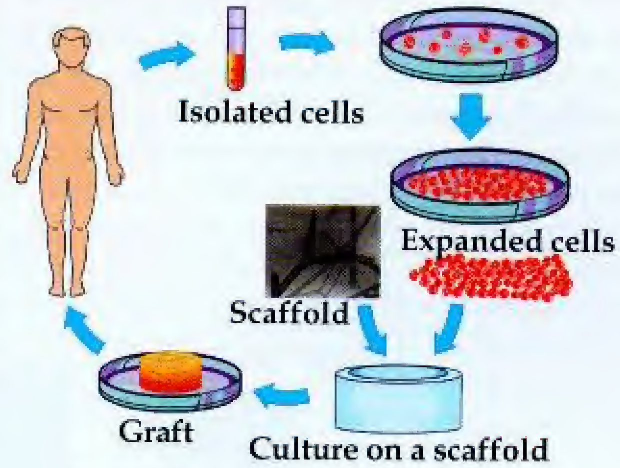
14.6 Tissue Engineering

Tissue engineering is emerging as an exciting option in healthcare to restore or replace damaged or injured anatomic structure, tissue or even organs. This new treatment applies the principles of biology and engineering to develop substitutes for damaged tissue that can carry out the functions of the original tissues. To do this successfully, tissue engineering must mimic tissue properties at the nanoscale.

According to Langer and Vacanti, pioneers in the field of tissue engineering, 'tissue engineering is an interdisciplinary field that applies the principles of engineering and life sciences toward development of biological substitutes that restore, maintain or improve tissue function or a whole organ'.

Tissue engineering has been made possible by advances in cell biology, molecular biology, genetics, biomedical engineering, material chemistry, material science and nanoscience and technology. Tissue engineering uses living cells as building blocks. Cells of skin, muscles, cartilage, bone marrow and of late stem cells of humans or animals grown in large scale culturing are used to replace the damaged tissues in human beings. Engineering principles are used to build

scaffolds or temporary structures made of naturally derived or easily biodegradable and biocompatible materials. The scaffolds are implanted at the required site in the body. A scaffold acts as a template where the body's own cells grow to form new tissues even as the scaffold is gradually absorbed by the body.



Basics of tissue engineering

The types of cells generally harvested for tissue engineering are:

Autologous cells. These are cells taken from an individual and reimplanted in the same individual.

Allogenic cells. These are cells from a donor belonging to the same species.

Xenogenic cells. These are cells from individuals belonging to another species.

Isogenic cells. These cells are from genetically identical organisms (twins, clones or inbred research animals).

Primary cells from an organism, **Secondary cells** (cells from a cell bank) and **Stem cells** are also used.

Scaffolds play a crucial role in tissue engineering. A scaffold is an artificial, three dimensional temporary structure that allows cells to create their own microenvironment. Cells are seeded or implanted close to each other into the scaffold and the cells deposit their own matrix inside the scaffold. As the scaffold degrades, the cells form a three dimensional tissue structure that mimics the natural tissues of the host body. For successful cell seeding and diffusion of both cells and nutrients throughout the scaffold necessary for tissue formation, the scaffold must be highly porous with adequately sized pores. The material from which the scaffold is fabricated must be both biocompatible to prevent rejection and biodegradable so that it can be absorbed by the body. Also, the rate at which the scaffold material degrades or breaks down must be as close as possible to the rate at which new cells or tissues are formed. Absorption of the scaffold material by the surrounding tissues is preferable as it prevents the need for surgical removal of the scaffold.

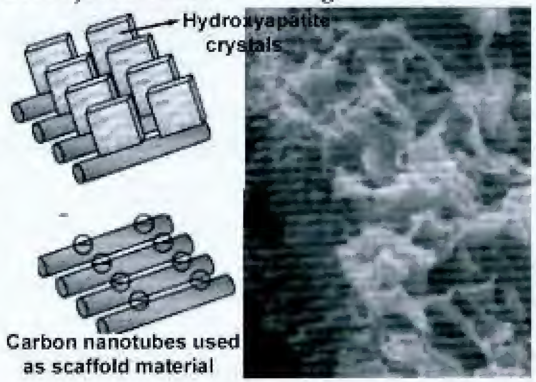


Figure shows carbon nanotubes and hydroxyapatite crystals in the mineralised bundle

Source: Bin Zhao et al., *Chem. Mater.* 2005

Carbon nanotubes can be used as scaffold material to heal broken bones as they have both high mechanical strength and flexibility. Carbon nanotubes can also mimic the role played by collagen fibers of the bone tissue and facilitate the growth of hydroxyapatite in the bone.

Tissue engineering is no longer a dream. It is quickly becoming a viable option in regenerative medicine. It is already used to replace skin lost due to burns or chronic ulcers, repair or even replace damaged or defective bones or cartilage and aged muscles. Replacement organs grown by tissue engineering using autologous or allogenic or isogenic cells as building materials will not be rejected by the immune system of the recipient.

Tissue engineering is a perfect venue for exploring the practical applications of nanotechnology. However, the following problems must be addressed before the potential medical benefits of tissue engineering can be fulfilled:

- technology to scale up cell culturing to produce cells in commercially viable quantities without the danger of contamination or genetic changes in the cells produced.
- appropriate fool proof techniques for long term storage of cells and tissues that can survive different environmental conditions.
- newer innovative technologies to develop and produce both naturally derived and synthetic biomaterials.
- cost effective technologies to produce tissue engineered replacement organs in large quantities.
- to develop multipotential universal donor cells that are not rejected by human recipients.

14.7 Silver nanoparticles and water purification

Water shortage and the resultant lack of access to safe drinking water has become a major global problem. Even when water

is available, it is often polluted with harmful bacteria and fungus, making it unsafe for human consumption.

Advances in preparation of nanomaterials, nanoabsorbents, bioactive nanoparticles, as well as nanoengineering provide effective solutions to the problems of purification of water. Nanomaterials like nanocarbon and nanosilver are used to purify water. Nanosilver is preferred because nanosilver particles disperse in water to form silver ions. Silver ions prevent bacteria and algae build up in water reservoirs, water tanks, community water systems.

Silver has been used for centuries as a means of purifying water and for preserving food before the use of silver nanoparticles. For example, Indians used thin silver foils to preserve food that spoiled easily. Even today, in certain parts of India, silver foil is used to cover sweets. Phoenicians kept water, wine and vinegar in silver vessels during their voyages. In America, early settlers moving westward put copper and silver coins in water casks to keep it potable during their long journey through water scarce regions. This is still a common practice for keeping water potable in remote areas.

Instead of silver coins, nanosilver is found to be better as it has extremely large surface area. This characteristic of silver nanoparticles increases their contact with bacteria and fungi thereby increasing their antibacterial and antifungal actions. When nanosilver particles come in contact with bacteria and fungi, they adversely affect their cellular metabolism and

suppress cellular respiration. They also adversely affect the transport of substrate in the cell membrane. Also, silver nanoparticles slow down the proliferation and growth of infection, odor and itchiness causing bacteria and fungi.

The following properties of nanosilver make it the material of choice for fabricating water purification devices. It is fast acting, nonpoisonous, nonstimulating, hydrophilic, gets easily dispersed in water. In addition, it does not cause allergies and is highly effective as bactericide and fungicide. Silver nanoparticle coated ceramic composites have wide application in water purification as it is very effective in preventing the growth of E coli bacteria. Bactericidal property of silver nanoparticles enables them to kill various harmful and disease causing bacteria such as salmonella, staphylococcus, Legionella pneumophilia (an aquatic organism which is commonly present in small quantities in natural water sources).

Water filters with silver nanoparticles coated on the inner porous surface of ceramic candles have been developed in India. Silver nanoparticles effectively kill disease causing bacteria in the water as it is filtered. The candles can be fitted into a variety of filter housing such as stainless steel filter housing or mud or clay filter housing. As the water flow in the filters is due to gravity, they do not require high water pressure or electricity to function. These filters offer a low cost and environmentally friendly solution to providing safe drinking water both in rural and urban areas.

Is silver the best "Swimming Pool" water purifier?

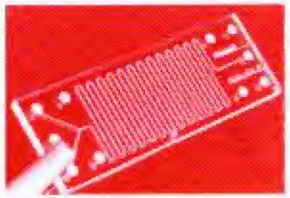
In April 1975, in Nebraska U.S.A., 50 gallons of untreated sewage plant effluent were pumped into a swimming pool

(20,000 gallon water) with no disinfectant in the water of the pool. This resulted in E coli cell concentration of 7,000 cells per 100 ml of water of the pool. The contaminated water from the pool was passed through a tank having alternate anodic and cathodic electrodes of silver for treatment. In less than three hours, the contaminated water from the pool was almost completely free of E coli!

It was concluded that purification of swimming pool water using silver was better than use of chlorine or other chemical as silver also destroyed pseudomonas and staphylococcus organisms.

Both NASA of USA and Russian Space agency have used ionized silver to provide safe and long-lasting means of transforming polluted waste water into pure water for drinking, air conditioning and food preparation on space shuttles.

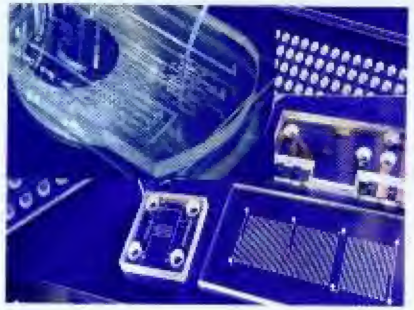
14.8 Lab-on-a-chip (LOC)



Lab-on-a-chip or LOC devices are integrated semiconductor devices that function as a laboratory for the testing and analysis of very small chemical, biological or clinical samples. The laboratory functions can be a single function or multiple functions and are integrated on a single chip measuring only a few millimeters or a few square centimeters. Lab on a chip device integrates fluidic elements, sensor components and detection elements which can perform a complete chemical reaction or analysis starting with sample preparation, chemical reactions, separation and finally

detection. Most lab-on-a chip products are designed to have capabilities for chemical or biological analysis. **Lab-on-a-chip devices are also referred to as 'microfluidics'.**

A gas chromatograph was the first LOC analysis system that was developed. It took another fifteen years for various devices such as micropumps, flowsensors and analysis systems based on integrated fluid treatments similar to the present Lab on a Chip devices to be developed.



LOC is not a nano device. In a LOC device, a network of channels for storing, mixing and testing chemical compounds are built on a semiconductor chip. This serves as a **micro or nano lab.** Lab-on-a-Chip (LOC) devices can handle only extremely small amounts of fluids such as blood and human serum. LOC is based on microfluidics devices technology. **Lab on a chip can be regarded as a scaled down version of microelectromechanical systems or MEMS.** The chip in a LOC has an on-chip library of reagents and computer controlled sequential microchannel switching controls. The chip selects the most appropriate reagent, the sampling and chemicals from the on- chip library and performs chemical reactions in minutes that would ordinarily take days or weeks in a traditional laboratory. Fabrication processes of most of the LOC devices are based on photolithography.

Lab-on-a-Chip devices can analyze more than 10 samples in less than 45 minutes. They are also easy to use. The person operating the device has to just load the chip and press the

start button for the device to start functioning. Other advantages of a LOC device include hardware free of contamination, reproducibility of data, low cost of fabrication and chip disposal. It is also easy to operate and store data.

Lab-on-a-Chip devices are used in chemistry, biology, medicine and nanotechnology. They are used for doing chemical analysis, chromatographic separation of samples, detection of bacteria and viruses and the analysis of proteins, DNA or RNA. Other Lab-on-a-Chip applications are biochemical assays, immunoassay, extraction of DNA by cracking of cells and single cell analysis.

14.9 Field Emission Flatbed-Display based on carbon nanotubes

Field emission is the emission of electrons from a solid under a strong electric field. When the field is enhanced at the tip of a sharp object, a high field is produced. A Flatbed Display Field Emission uses a flat panel display technology. This technology consists of a large-area field electron source and a coloured phosphor screen. The electrons from the field emission source strike the green phosphor screen to produce coloured images.

CNT based display

A Field Emission Display (FED) consists of a rectangular array of cathode ray tubes (CRTs). Each CRT of the array produces a single sub-pixel. When three of them are

grouped together, they produce RGB (red-green-blue) pixels. The FEDs have a high contrast level and a fast response. A major advantage of flat panels or flat bed technologies is that they require less than 50% power than CRTs as they do not require heat to emit electrons from the surface of the source. The most common flat screen display at present is the LCD display. Originally, thin silicon (Si) or tungsten (W) were used as tips and attempts are now being made to use carbon nanotubes (CNTs) as tips.

Tungsten tip coated with carbon nanotubes

CNT tips have the following advantages over metallic tips. The radius of curvature at the CNT tip is very small due to CNT's high aspect ratio i.e. carbon nanotubes can have diameters anywhere between 1 nm and 100 nm and their lengths can be several microns. Their strong covalent bonds make them both chemically inert to poisoning and physically inert to sputtering during field emission. They are chemically stable and mechanically strong, and are capable of carrying strong current before the migration of electrons. Also, when high currents are passed through them, the CNT tips unlike

metallic tips do not undergo field induced sharpening. A great advantage of CNT emitters is that they do not require high vacuum conditions and high energy sources that thermionic emitters like CRTs and LCD technologies require. They can operate stably even at moderate vacuum conditions. The nanotubes are usually arranged into an array to allow large amount of current to pass through. This is necessary as the extremely small cross section of a nanotube allows the emission of only a small amount of current through it.

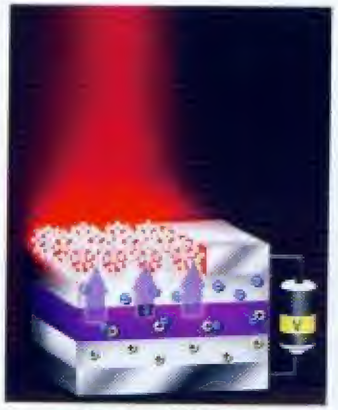
If high field emission at low voltages is required, alignment of nanotubes becomes extremely crucial. In these circumstances, the nanotubes must be aligned perpendicular to the voltage source (substrate or surface).

14.10 Nanotechnology and future of lighting

Lighting all over the world mostly uses various versions of the electric bulb invented by Edison more than a century ago. These incandescent bulbs waste enormous quantities of electricity as their filament converts heat energy to light energy. Also, as this electricity is produced either by burning coal or petroleum, it contributes to global warming by adding millions of tons of carbon emissions and green house gases to the atmosphere. Future light sources will not be incandescent bulbs.

Nanotechnology driven solid state **light emitting diodes (LEDs) and OLEDs (organic light emitting diodes)** are set to provide cheaper, longer lasting, energy efficient and environmentally friendly light sources by considerably reducing energy consumption and emission of green house gases. They will revolutionise lighting technology by

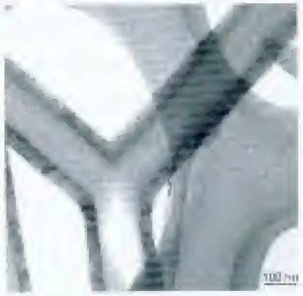
introducing flexible and miniature devices that can provide extremely bright light. OLED devices use phosphorescent metal complexes that emit sustained light when they are stimulated by an electric voltage. OLEDs do not need back lights (as LCDs do) as they create their own light. Therefore their consumption of power is very low. We already see LEDs as light sources in traffic signals, flashlights and even architectural lighting. Even though LEDs have the potential to become the major light source in the long run, it has to overcome certain major drawbacks. Commercially available LEDs are less efficient than Compact fluorescent light (CFL), cost much more than CFL and their color is not pure white. Most LEDs emit cool bluish white or **lunar white** light. However, researchers have succeeded in creating white light by coating blue LEDs with a layer of nanocrystals of core cadmium selenide with a surrounding layer of zinc sulfide. The nanocrystals emit their own red and green light but absorb some of the blue light emitted by the LED. The red and green light emitted by the nanocrystals then combine with the remaining blue light and produce warm white light. Commercially available LEDs producing white light are also based on LEDs that emit a bluish white glow. These use gallium nitride nanostructures which emit blue light on excitation. By using an yellow phosphor coating, the blue light is converted to blue-tinged white light.



Nano LED's

14.11 Nanocomputers

A nanocomputer is a computer whose basic parts are only a few nanometers in size. Nanocomputers use nano-electronics to fabricate transistors and 'logic gates' and integrated circuits.

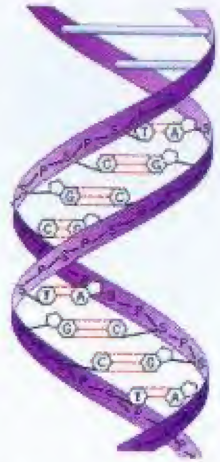


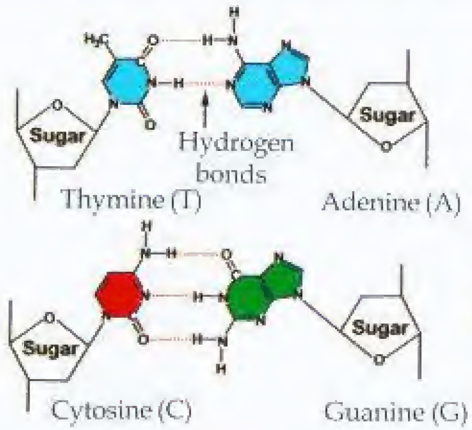
Nano integrated circuits of nanocomputers are so minute that they are not visible to the naked eye. They require sophisticated microscopes to see! The integrated circuits of a nanocomputer aims to process individual electrons. Nano integrated circuits perforce will require nano logic devices that can count single electrons. **Y junction carbon nanotubes** have been used as transistors in fabricating a nanocomputer. A nanocomputer can be electronic nanocomputer, mechanical nanocomputer, chemical nanocomputer, biochemical or bio-organic nanocomputer and quantum nanocomputer.

Nano integrated circuits of electronic nanocomputer are fabricated by using nanolithography. A mechanical nanocomputer uses nanogears, a chemical nanocomputer uses chemical structures and interactions, a biochemical or bio-organic nanocomputer uses DNA as the chip. At present, transistors used in the processors are approaching 45 nm in size. As further miniaturization looks unlikely, nanocomputers with their computing components only a few nanometer offer immense possibilities for storing vast quantities of data and

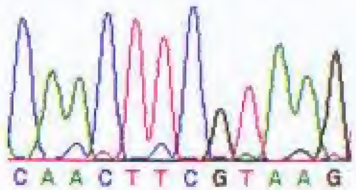
fast retrieval of stored data with little power consumption. However, major problems like manufacturing components on a molecular scale and assembling them to actually construct a working nanocomputer have to be solved before nanocomputers become a reality.

DNA computer: A DNA computer is a nanocomputer that uses the DNA molecule to store information or data and to perform complex tasks and provide possible solutions to the original problem. DNA computing is a new and exciting interdisciplinary field. It involves research in both molecular biology and computer science. The idea of a DNA- based computer may be considered as an attempt to mimic nature. DNA or biochemical nanocomputers are present in living organisms (including us) storing vast quantities of data and continuously performing complex tasks but they generally cannot be controlled or manipulated by us.





Complementarity in DNA sequences makes it possible to have an enormous data density.



In a cell, a variety of enzymes which can be compared to small protein (molecular) machines modify the DNA. These machines in the cell read and process the information in the DNA. Biochemical reactions or functions do not occur sequentially or one at a time but occur parallely and simultaneously. The power for these reactions to occur comes from the DNA molecule itself.

Scientists have used these unique features in building DNA computers. The DNA molecule is programmed or the problem to be solved is coded into a DNA sequence. The programmed DNA or the DNA sequence is put together with enzymes in a test tube. The scientists instruct the protein machines what reactions to perform by controlling the composition of the DNA molecule.

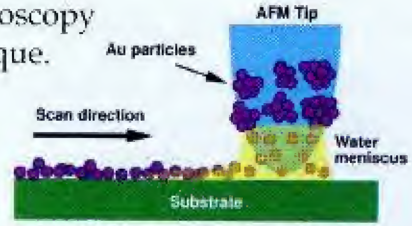
In a DNA computer, DNA is analogous to the software in a conventional computer and enzymes to the hardware. The computer is so small that it cannot be seen by the naked eye (~one trillion DNA computers would fit into a drop of the solution). In fact, the solution in the test tube with the DNA computer looks like water. The solution to the problem (the input) does not appear on the computer screen. Instead, they are analyzed using specially developed tools and techniques that enable the scientists to see and increase the length of the output DNA molecule. Once the coded problem, the DNA molecule and enzyme molecules are put together in a solution in a test tube and mixed, the computer operates without any further human intervention. If the output is to be seen by the naked eye, outside manipulation becomes necessary.

DNA computing has the advantages of parallel processing, density of data storage, speed of operations. Also, there is no need for external power or energy as the required fuel is

provided by the DNA molecule itself. DNA computers have exciting possibilities in the medical field.

14.12 Dip Pen Nanolithography (DPN) with nanocrystals

This is an Atomic Force Microscopy based nanofabrication technique. In this technique, the tip of the AFM delivers the molecules or particles onto a surface via a water or a solvent meniscus. DPN



Dip Pen lithography

technique then creates nanometric surface patterning on the substrate. In DPN technology, the cantilever tip of AFM functions as a pen. When the tip or pen comes in contact with the substrate (or paper) the nib of the pen deposits the coated molecules or the chemical

compound or mixture (or the ink) onto the substrate (paper). In addition to the water meniscus, a variety of solvent meniscus or inks like biomolecules meniscus, organic molecules meniscus or inorganic meniscus can be used to create patterns of nanometric size on a variety of substrates.

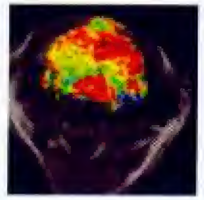
The quality and the stability of the nanostructures created by DPN depend upon a number of factors. Apart from temperature, humidity, speed at which the tip moves, the strength of adhesion of the deposited material, adhesion between the AFM tip and the ink or material to be deposited, also affect the nanostructures created on the substrate.

DPN technology is a versatile technology as it can be used for creating nanostructures on the substrate, for imaging and reading them (using an AFM). It is an invaluable tool for studying the basic problems in surface science and materials chemistry.

14.13 MRI with magnetic nanoparticles

Magnetic Resonance Imaging or **MRI** is an imaging technique used to 'see' the internal structure and function of the body. It is a particularly useful imaging technique to build up an image of soft tissues. As MRI scans, it uses radiowave energy and the magnetic field to build a picture of the tissues in the selected location in the body. To obtain clear and sharp images, a contrasting agent is used. Nanoparticles and nanodevices are very effective as contrasting agents to increase the brightness of the image of the targetted region. Nanodevices made of biocompatible nanomaterials or nanoparticles are injected into the body of the patient. MRI can be used to monitor the working of nanodevices inside the body.

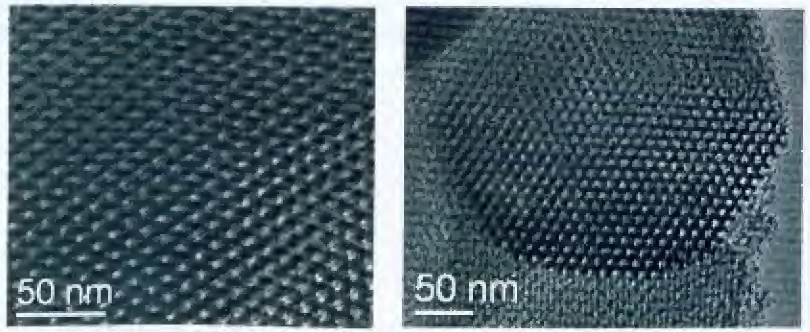
Medical nanodevices or a few nanoparticles are first injected intravenously into the body of the patient. The doctor then monitors their progress inside the patient's body and makes sure that the nanodevice or particles reach the location targetted for treatment.



Dyes are used to color the cells as it is difficult to track the cells. Quantum dots are attached to proteins that penetrate cell walls. The quantum dots can be of different sizes and made of bio-inert material but they must demonstrate the nanoscale property that is color dependent. Nanoparticles of manganese oxide have been used as contrast agents for magnetic resonance imaging (MRI). Manganese oxide nanoparticles allow doctors to 'see' inside living brain tissues in the same detail as dissected tissues viewed under a microscope. Manganese oxide as the contrasting agent is also effective for liver, kidney and spinal imaging. Nanoparticles of magnetite (Fe_3O_4) and other ferrites are also likely to be of use in MRI.

14.14 Nanoporous solids and nanocatalysis

Nanoporous solids or nanoporous materials contain nanometric pores. Generally the size of the holes is less than 100 nm. Nanoporous solids contain inorganic or hybrid organic-inorganic frameworks with pores whose size can be manipulated. They have a large surface area. The framework



TEM images of nanoporous silica

is responsible for the magnetic, optical, electrical and other physical properties of the material.

The nanopores are the sites of reactions and of separation and storage. The internal surface area contributes to the catalytic property of the nanoporous solid. Nanoporous materials are found in naturally occurring minerals as well as in biological systems in nature. Naturally occurring zeolite is an example of nanoporous mineral and our cells are classic examples of nanoporous material in biological system. Invention of various microscopes and other powerful tools have enabled scientists to create designer nanoporous solids. Nanoporous solids have been made in the laboratory out of a variety of substances such as silicates and phosphates. They have also been made out of carbon, metals and some organic materials.

Nanopores can be created by combining etching with soft lithography or by employing traditional lithography. Nanoporous silicon can be made by etching silicon with acid. They can also be prepared by selectively leaching out the unwanted substance from the selected solid without displacing pores from their place, by heating a combination of polymers so that one polymer degrades and escapes leaving a nanoporous solid. Sol-gel method is useful for preparing aerogels where a gas is dispersed in a gel. Aerogels are very light and are highly porous.

Activated carbon is a nanoporous material. It is obtained by processing carbon containing materials. The resultant carbon is extremely porous. Due to its high degree of porosity activated carbon has a very large surface area. Just one gram of the material has approximately $500m^2$ surface area. Chemical reactions and adsorption take place in the available large surface area. Activated carbon has a wide variety of

applications. It is extensively used in purification of certain gases, gold and water, extraction of certain metals, sewage treatment plants, air filters and gas masks. Zeolites have been used as catalytic agents in petroleum industry.

Catalysis using nanoparticles of metals and other inorganic substances is by no means new. Much before nanoscience became popular, chemists have used nanomaterials as catalysts in heterogeneous reactions. The subject has become more interesting in the last few years due to the discovery of new properties associated with nanoparticles of gold and other materials. For example, catalysis using gold nanoparticles has become an important area of research.

Concluding Remarks

As discussed in earlier sections, nanoscience and technology has advanced considerably in the last 5 to 6 years and many of the applications of nanomaterials have become realities. The future of nanoscience and technology promises to be bright. Many more of the novel properties of the nanomaterials will certainly be put to use for a variety of applications.

There are many aspects of nanoscience and nanotechnology that are yet to be explored fully and there are many challenging aspects where further research and development efforts are necessary. It would be particularly exciting if electronic devices and computers based on nanotubes and other materials become a reality in the next 5-10 years. We can imagine a day when we can readily grow the spinal chord or artificial skin to replace damaged ones. There is a crucial need to investigate the toxicological effects of nanomaterials.

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